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The Aqueous Zinc Chloride System and its Complex Formation with Cellulose-Related Compounds

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THE AQUEOUS ZINC CHLORIDE SYSTEM AND ITS COMPLEX FORMATION WITH CELLULOSE-RELATED COMPOUNDS

A thesis submitted by

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SUMMARY

Complex formation between aqueous zinc chloride and various cellulose-related polyhydroxy compounds was investigated.

NMR chemical shift measurements and the method of continuous variations using optical rotation measurements at 546 nm. were employed to detect complex formation in aqueous solutions of zinc chloride below 3M. Complex formation occurred with methyl β-D-glucopyranoside, methyl α-D-glucopyranoside, methyl 6-deoxy-β-D-glucopyranoside, methyl 4,6-di-O-methyl-β-D-glucopyranoside, methyl β-D-xylopyranoside, myo-inositol, sorbitol, and glycerol with a 1:1 molar ratio of salt to model compound. Little or no complex formation was observed for methyl 3-O-methyl-(α,β)-D-glucopyranoside, methyl 2,3,4,6-tetra-O-methyl-β-D-glucopyranoside, ethyl 3,4,6-tri-O-methyl-β-D-glucopyranoside, hexa-O-methyl-myo-inositol, ethylene glycol, methyl cellosolve, ethanol, or n-propanol. These results indicate that zinc chloride complexes with vicinal hydroxyls on certain model compounds; in dilute solutions the methoxyl group blocks this reaction. In addition to the required vicinal hydroxyls, other oxygen atoms are needed to confer water solubility on the complex. Compounds which contain both vicinal hydroxyls and extra oxygen complex well with zinc chloride. Those which contain vicinal hydroxyls and no additional oxygen or contain no vicinal hydroxyls exhibit little or no complex formation.

The method of attenuated total reflectance (ATR) was used to obtain the infrared spectra (3000-800 $cm.^{-1}$) of methyl β-D-glucopyranoside in 3-11M zinc chloride solutions. Below 3M there was essentially no change in the ATR spectra, but above 3M there were increasing frequency shifts in the absorption peaks from 1100-950 $cm.^{-1}$, and at concentrations greater than 8M a weak, broad absorption maximum appeared at 870 $cm.^{-1}$. At 9.5M zinc chloride the ATR spectra of methyl 2,3,4,6-tetra-O-methyl-β-D-glucopyranoside and hexa-O-methyl-myo-inositol exhibited

frequency shifts and new absorption maxima appeared at 910-835 cm.$^{-1}$, indicating that the methoxyl group does not block complex formation in concentrated zinc chloride solutions. The change of the NMR chemical shifts of methyl β-D-glucopyranoside in deuterated zinc chloride solutions was independent of the temperature below 7M, but above 7M it was increasingly dependent on temperature. The difference between the calculated and observed ultraviolet absorbances (257 nm.) of mixtures of methyl β-D-glucopyranoside and zinc chloride was negligible below 7M zinc chloride, but above 7M there were increasing differences. These results indicate that the concentration and the stability of the complex increase as the zinc chloride concentration is raised.

The above results indicate that the probable swelling mechanism for cellulose in aqueous zinc chloride solutions depends on the formation of a complex with a vicinal pair of hydroxyls on carbon atoms two and three of the glucopyranoside repeating unit. Although complex formation is weak at dilute concentrations, the concentration and stability of the complex increase as the zinc chloride concentration is increased. Above 8M zinc chloride there is insufficient water to hydrate the zinc ions in solution. This causes a ligand deficiency relative to the zinc which causes the stability of the complex to increase markedly above 8M, and is responsible for the large increases in swelling and crystallinity loss of cellulose in zinc chloride solutions above 8M. As the water shortage becomes more severe (about 10M) the zinc chloride associates to form a polymeric aggregate which causes the viscosity of the aqueous zinc chloride solutions to increase markedly. The formation of the polymeric aggregate is responsible for the decrease in swelling and crystallinity loss above 10M.

INTRODUCTION

In spite of the many studies, much controversy exists as to the mechanism of swelling of cellulose in zinc chloride solutions. Through the study of the complex formation of zinc chloride with the methyl glucopyranosides and other cellulose-related compounds, this thesis seeks to further clarify the phenomena which are observed when aqueous zinc chloride is contacted with cellulose.

EFFECT OF ZINC CHLORIDE ON CELLULOSE

Treatment of cellulose with concentrated aqueous zinc chloride solutions (63-72% by wt.) causes a mercerizing effect, strong swelling, a capacity for being hydrolyzed, a slight rise in the copper number, and a slightly raised but still low alkali solubility (1). Paper after treatment with a concentrated solution of aqueous zinc chloride has decreased porosity, increased density, stiffness, and durability. It also has the toughness, semitransparency, and general appearance of parchment (2).

An examination of the swelling (3) and crystallinity (4) of cellulose in aqueous zinc chloride solutions demonstrated a marked concentration dependency for these phenomena. Cellulose swelled only slightly more in dilute zinc chloride solutions up to about 30% (by wt.) than it did in water. Higher concentrations caused increasing swelling reaching a maximum of 13,000% (weight basis) at 63-73% zinc chloride. Above 73% the swelling decreased rapidly to a value at 75-76% which was essentially the same as in dilute solutions of zinc chloride. From 0-52% zinc chloride, essentially no change in the crystallinity was observed. From 52-58% there was a slight increase in the crystallinity. From 58-75% the crystallinity was drastically reduced, but above 75% the crystallinity was the same as in dilute solutions. It was concluded that zinc chloride was an intracrystalline swelling agent only in the 58-74% concentration range.

EFFECT OF OTHER NEUTRAL SALTS ON CELLULOSE

The term, neutral salt, is defined in this thesis as a metal-nonmetal compound that does not possess an ionizable proton or hydroxyl group.

Kasbekar (5) has reviewed the work concerning the effect of neutral salt solutions on cellulose.

Wiemarn (6) investigated the swelling and dispersion of cellulose in several neutral salt solutions and concluded that it is possible to gelatinize cellulose if proper conditions of temperature, pressure, and concentration are maintained. The most efficient salts were those which were most easily hydrated and which possessed the greatest solubility in water.

This agrees with the work of Stamm (7) who found that the decreasing order of swelling was also the order of decreasing solubility in equivalents per liter, decreasing specific volume of the salt in solution, decreasing surface tension, and increasing vapor pressure of water over the solution. The pH of the solution had practically no effect on the swelling.

AQUEOUS ZINC CHLORIDE SYSTEM

Abnormal activity coefficients (8,9) and transference numbers (10) indicate complex ionic association even in dilute aqueous solutions of zinc chloride.

Raman studies (11,12) of aqueous zinc chloride solutions indicated the presence of $Zn(H_2O)_6^{++}$, $ZnCl_4(H_2O)_2^{--}$, $ZnCl^+$(aq.), and $ZnCl_2$(aq.) at concentrations less than ten molar (~70%). From ~0.5 to ~10M zinc chloride, about 25-40% of the zinc molecules were present in the tetrachloro complex. The concentrations of $ZnCl^+$(aq.) and $ZnCl_2$(aq.) were small. Significant amounts of $ZnCl^+$(aq.) were

observed below 4M. Above 4M the $ZnCl^{+}$(aq.) was replaced by $ZnCl_2$(aq.). For stoichiometric solutions greater than ten molar, the evidence suggested the formation of a polymeric species or aggregate with structural characteristics similar to those found in the crystal. This was also indicated by the viscosity of the zinc chloride solutions which increased rapidly above ten molar.

Aqueous solutions of zinc chloride reacted acid until diluted below about 3-4N (13), and the pH decreased with increasing concentration. A zinc oxychloride precipitate occurred in basic solutions if zinc oxide was present; that is, in solutions less than 3-4N (~20%).

METAL-CARBOHYDRATE COMPLEXES

The existence of complexes between salts of sodium, lithium, barium, calcium, strontium, and carbohydrates has been established by deviations from normal behavior of solubility, optical rotation, conductivity, and other data (14).

Malcolm (15) has determined stability constants for borate-carbohydrate complexes formed in an aqueous medium. Kraske (16) obtained spectrophotometric evidence for complex formation of the ferric ion with glucose and cellobiose in aqueous solution. Snell (17) observed that the vapor pressure of water over a solution of zinc sulfate increased with the addition of glucose, which indicated formation of a complex between zinc sulfate and glucose.

Of particular interest to this thesis is the work of Reeves (18) and Bayer (19) who determined the cellulose dissolving mechanism of copper and iron-based solvents, respectively. This was done by studying the complex formation of cuprammonium hydroxide and ferric iron tartrate with cellulose-related model compounds; primarily, methyl glycopyranosides. They demonstrated that formation of a metal

chelate with a pair of hydroxyls on the glucopyranoside ring is a necessary step in the cellulose-dissolving mechanism.

COMPLEXING ABILITY OF ZINC

The ability of transition metals to form complexes with molecules having available electron pairs is well known (20). In general, the chemical behavior of the Zn^{++} ion shows many resemblances to the divalent ions of the first transition series, which immediately precedes it. Although it is not so strong a complex former as these ions, it is chemically more similar to them than to gallium on one hand or magnesium and calcium (which have similar ionic radii) on the other. Undoubtedly the 4s and 4p orbitals of Zn^{++} are not greatly different from those of the preceding transition elements in energy and other characteristics. The factor which tends to set Zn^{++} apart from all the immediately preceding divalent ions is the lack of any vacancies in the underlying 3d shell. The major effect of this difference is only stereochemical. The Zn^{++} ion does not exhibit the intrinsic tendency to form octahedral complexes which is dominant in the first transition metal series; it may have octahedral, planar, or tetrahedral coordination depending on the nature of the coordinated group and the effect of external forces. The ability of Zn^{++} to form complexes with many compounds is well known in spite of a completely filled 3d shell (21,22).

STATEMENT OF THE PROBLEM

From the above discussion it is seen that zinc chloride would probably complex with carbohydrates. Any complex formation would probably be very concentration-dependent due to the marked changes with concentration of the aqueous zinc chloride system.

With the above in mind, the goals of this research were as follows:

(1) Determine whether or not a complex between zinc chloride and cellulose-related polyhydroxy compounds exists (e.g., methyl glucopyranosides and other compounds containing vicinal hydroxyls).

(2) Determine the effect of zinc chloride concentration on complex formation.

(3) Locate the points of complexing on the glucopyranoside ring.

(4) Infer from the study of model compounds the probable cellulose swelling mechanism.

RESULTS AND DISCUSSION

Experimental details are given under "Experimental Procedures and Techniques" which follows the discussion of results. The raw data, analysis of experimental error, and sample calculations are presented in Appendices I, III, and IV, respectively. Sample NMR, infrared, and ultraviolet spectra are given in Appendix V.

COMPLEX FORMATION BETWEEN ZINC CHLORIDE AND METHYL β-D-GLUCOPYRANOSIDE

Methyl β-D-glucopyranoside was chosen as representative of the cellulose-related compounds which would be expected to exhibit complex formation with zinc chloride. Complexing with other model compounds is discussed in later sections.

Establishing that there is a complex between methyl β-D-glucopyranoside and zinc chloride was accomplished by the method of continuous variations, by NMR chemical shift measurements, and by ultraviolet absorbance measurements. These methods all reflect a change in the electronic distribution of the model compound and zinc chloride, which is attributed to the formation of a complex between them.

Continuous variations measurements of methyl β-D-glucopyranoside and zinc chloride from 0-2.5M showed a maximum deviation of 0.60 and 0.86 degrees* from expected optical rotation values in an equimolar solution of the salt and the carbohydrate at 546 and 435.8 nm., respectively. Since the optical activity of methyl β-D-glucopyranoside arises from the asymmetric electronic distribution about asymmetric carbon atoms within the sugar, this deviation from expected behavior is indicative of a change in the electronic distribution about these asymmetric centers.

*Any deviation greater than 0.08 degrees is significant at the 95% confidence level (Appendix III).

The NMR spectrum of 1.0M methyl β-D-glucopyranoside in a 1.0M zinc chloride solution (in D_2O) compared to its spectrum without zinc chloride, exhibited chemical shift changes ($\Delta\nu$) of 2.05 and 1.85 c.p.s.* for the anomeric proton (H_1) and the remaining ring protons ($_{2,3,4,5}$), respectively. The chemical shift arises from the diamagnetic shielding of the electrons surrounding a hydrogen nucleus. Therefore, the changes in the chemical shifts reflected a change in the electronic distribution about that nucleus.

Using a ten centimeter cell, methyl β-D-glucopyranoside exhibited a weak general absorption in the ultraviolet region (220-340 nm.) with no distinguishable peaks. However, zinc chloride had an absorption maximum at 257 nm. When an equimolar (1.0M) zinc chloride and methyl β-D-glucopyranoside solution was prepared, the observed absorbance (10 centimeter path) of the mixture at 257 nm. was 0.055 absorbance unit less than the value calculated from the pure component solutions. This indicates an electronic charge transfer between the zinc chloride species and the sugar molecule.

EFFECT OF ZINC CHLORIDE CONCENTRATION ON COMPLEX FORMATION

Two experimental restrictions are encountered when the zinc chloride concentration is increased. Aqueous solubility limits for most of the model compounds eliminate the method of continuous variations at concentrations greater than about 3.0M. Above 1.5M zinc chloride the change ($\Delta\nu$) in the NMR chemical shifts of the model compounds exhibit a partial dependency on the zinc chloride concentration which is primarily related to the change in the polarity of the solution; i.e., a solvent effect independent of complex formation. Below 1.5M zinc chloride the solvent effect is negligible for most of the model compounds.

*Analysis of experimental error indicated that any deviation greater than 0.32 c.p.s. is significant at the 95% confidence level (Appendix III). The chemical shift change was positive for a downfield shift and negative for an upfield shift.

The method of attenuated total reflectance (ATR) was used to obtain infrared spectra (3000-800 cm.$^{-1}$) of methyl β-D-glucopyranoside in varying concentrations of zinc chloride (3-11.5M). The results are presented in Table I.

TABLE I

INFRARED SPECTRA OF METHYL β-D-GLUCOPYRANOSIDE IN VARIOUS AQUEOUS ZINC CHLORIDE SOLUTIONS

Zinc Chloride Molarity	Frequencies of Absorption Maxima, cm.$^{-1}$					
0.0	1440	1390	1075	1031	993	--
3.0	1440	1390	1073	1030	990	--
5.0	1440	1390	1072	1020	987	--
6.0	1440	1390	1072	1021	990	--
7.0	1440	1390	1069	1015	990	--
8.0	1440	1390	1069	1015	985	870
9.0	1440	1390	1066	1013	986	870
9.5	1440	1390	1068	1010	987	870
10.0	1440	1390	1069	1010	985	870
11.5	1440	1390	1069	1010	985	870

The ATR spectrum of methyl β-D-glucopyranoside in 3.0M zinc chloride was essentially the same as the control without zinc chloride. As the zinc chloride concentration was increased above 3.0M there were increasing frequency shifts in the absorption peaks representing the carbon-oxygen stretching vibrations (1100-950 cm.$^{-1}$), and at concentrations greater than 8.0M a weak, broad absorption maximum appeared at 870 cm.$^{-1}$, which disappeared with dilution below 8.0M zinc chloride, indicating an easily reversible phenomenon. Also, above 7.0M zinc chloride the absorption at 1440 and 1390 cm.$^{-1}$ increased compared to the control without zinc chloride.

Although there were no changes in the optical rotations or NMR spectra of methyl 2,3,4,6-tetra-O-methyl-β-D-glucopyranoside or hexa-O-methyl-myo-inositol in zinc chloride solutions below 3.0M, at 9.5M the ATR spectra of these two compounds exhibited frequency shifts in the absorption peaks representing the carbon-oxygen stretching vibrations, and new absorption maxima appeared in the 910-835 cm.$^{-1}$

range, indicating that the methoxyl group does not block complex formation in concentrated zinc chloride solutions.

It has been demonstrated with various mono- and disaccharides that the infrared region, in which these frequency shifts and new absorption maxima occurred is very sensitive to stereochemical changes (23). The changes in the infrared spectra of the above compounds are attributed to alterations in the stereochemical properties caused by complex formation with zinc chloride. Since infrared absorption characteristic of the zinc-oxygen bond occurs in the 300-500 $cm.^{-1}$ region (24), the appearance of new absorption maxima in the 910-835 $cm.^{-1}$ region cannot be attributed directly to a zinc-oxygen bond.

Although the change ($\Delta\nu$) of the NMR chemical shift of the model compounds in zinc chloride solutions is partially dependent on the dielectric properties of the solution at greater than 1.5M zinc chloride, this solvent effect was circumvented by measuring the effect of temperature on $\Delta\nu$ as a function of the zinc chloride concentration. The effect of temperature on $\Delta\nu$ is shown below to be indicative of complex stability and independent of the solvent effect.

The term "stability" describes the bonding that occurs between reacting species; the stronger the bond, the more stable the complex. This is reflected by an increase in the equilibrium (stability) constant.

The effect of temperature on $\Delta\nu$ of the peaks representing the anomeric (H_1) and the other ring protons ($H_{2,3,4,5}$) of methyl β-D-glucopyranoside in varying concentrations of zinc chloride is presented in Table II. Below 7.0M zinc chloride no temperature dependence was observed for $\Delta\nu$ of the peaks representing the anomeric or the other ring protons, but at 7.0M there is a slight dependence of the $\Delta\nu$ value for the peak representing the ring protons ($H_{2,3,4,5}$). From 7.0-9.0M there is an

increasing dependence of $\Delta\nu$ on temperature for all protons. The nearly zero change from 60-77°C. as compared to the change from 43-60°C. was verified by duplicate experimental measurements.

TABLE II

TEMPERATURE DEPENDENCY OF THE CHANGE ($\Delta\nu$) OF THE NMR CHEMICAL SHIFTS OF METHYL β-D-GLUCOPYRANOSIDE IN ZINC CHLORIDE SOLUTIONS

Zinc Chloride Molarity	Chemical Shift Changes, c.p.s. Anomeric Proton (H_1)			Ring Protons ($H_{2,3,4,5}$)		
	42°C.	47°C.	68°C.	42°C.	47°C.	68°C.
0.0	0.00	0.00	0.00	0.00	0.00	0.00
7.0	7.04	7.25	6.94	8.00	8.06	7.52
	43°C.	60°C.	77°C.	43°C.	60°C.	77°C.
0.0	0.00	0.00	0.00	0.00	0.00	0.00
8.0	8.31	7.34	7.00	9.91	8.19	7.87
8.5	8.87	8.06	8.06	--	--	--
9.0	9.50	8.34	8.38	--	--	--

An assembly of magnetic nuclei, each with spin $\underline{I}$ and nuclear moment μ_o in a magnetic field $\underline{H}$ will absorb energy at a frequency given by (25)

$$\nu = g \mu_o H/hI \qquad (1)$$

where $\underline{g}$ and $\underline{h}$ are constants for a given nucleus. In an applied field $\underline{H_o}$ the electrons precess about the field direction and create circulating electric current which oppose $\underline{H_o}$. This gives rise to the following situation. From Equation (1), $\underline{H}$ is the magnetic field strength at the nucleus and differs from $\underline{H_o}$, the applied field, by an amount $\underline{H'}$;

$$H = H_o - H^1 \qquad (2)$$

$$H = (1-\sigma)\, H_o \qquad (3)$$

where σ is a dimensionless number known as the shielding coefficient or constant. Since $\underline{g}$, μ_o, $\underline{h}$, and $\underline{I}$ are constants for a given nucleus, then for the hydrogen nucleus from Equations (1) and (3)

$$\nu = (1-\sigma)\, \nu_o \qquad (4)$$

and

$$\Delta\nu = -\nu_o\, (\Delta\sigma) \qquad (5)$$

where ν_o is the frequency of the applied field $\underline{H}_o$.

At a given temperature and zinc chloride concentration $\Delta\nu$ may be separated into two components; (1) that due to complex formation, $\Delta\nu_{\underline{c}}$, and (2) that due to a change in solution properties, $\Delta\nu_{\underline{s}}$, i.e., a solvent effect.

$$\Delta\nu = \Delta\nu_c + \Delta\nu_s. \qquad (6)$$

The effect of a polar solvent on the NMR chemical shift may be represented as a function of the dielectric constant of the solvent, ε, the permanent dipole moment, μ, the optical polarizability, α, the refractive index, $\underline{n}$, and the average molecular radius, $\underline{r}$, of the model compound, and the angle between the permanent dipole moment and the carbon-hydrogen bond in consideration, cos ϕ, (26-27).

$$-\frac{\Delta\nu}{\nu_o} = \Delta\sigma = -2 \times 10^{-12} \left[\Delta\left(\frac{(\varepsilon-1)}{(2\varepsilon+n^2)}\right)\right]\frac{\mu}{\alpha}\cos\phi - 10^{-18}\left[\Delta\left(\frac{(\varepsilon-1)}{(2\varepsilon+n^2)}\right)\right]\frac{\mu^2}{\alpha^2} \qquad (7)$$

where $\alpha = (\underline{n}^2-1)\underline{r}^3/(\underline{n}^2+2)$.

Although the dielectric constant is appreciably temperature dependent, it may be demonstrated that the change in the ratio $(\varepsilon-1)/(2\varepsilon+\underline{n}^2)$ with temperature

is negligible (Appendix IV). Therefore, $\Delta\nu_s$ would be independent of temperature and the apparent effect of temperature would be to reduce $\Delta\nu_c$. Since $d(\Delta\nu)/dt$ is related to complex stability (28), the increase in $d(\Delta\nu)/dt$ above 7.0M was concluded to be an indication of increased complex stability. However, there are two reservations to this conclusion; (1) Although $\Delta\nu$ was measured relative to a control at the same temperature, there is the possibility that $d(\Delta\nu)/dt$ for an uncomplexed molecule is different from $d(\Delta\nu)/dt$ for a complexed molecule. (2) The near zero change in $\Delta\nu$ from 60-77°C. cannot be explained. These two factors suggest that temperature changes might affect the chemical shift in some manner not related to complex formation.

Evidence for increased complex concentration with increased zinc chloride concentration was demonstrated by the ultraviolet absorbance data for zinc chloride and methyl β-D-glucopyranoside which is presented in Table III.

TABLE III

ULTRAVIOLET ABSORBANCES FOR MIXTURES OF METHYL β-D-GLUCOPYRANOSIDE[a] AND ZINC CHLORIDE

Zinc Chloride Molarity	Absorbances (at 257 nm.) Observed	Calculated	Deviation
3.0	0.20	0.19	0.01
5.0	0.32	0.32	0.00
6.0	0.40	0.39	0.01
7.0	0.59	0.61	-0.02
9.0	1.01	0.89	0.12
10.0	1.21	1.00	0.21

[a]The methyl β-D-glucopyranoside concentration was constant at 0.5M.

Using a one centimeter path, the difference between calculated and observed absorbances for mixtures of methyl β-D-glucopyranoside and zinc chloride at or below 7.0M zinc chloride were negligible. Above this concentration there were increasing

differences, indicating an increased amount of electronic charge transfer which was attributed to an increase in the concentration of the complex.

On the premise that increased alteration of the physical properties of the model compounds in zinc chloride solutions is indicative of increased complex formation, it was concluded that the above results with ATR, NMR, and U.V. spectra indicate that the concentration of the complex and its stability increases as the zinc chloride concentration is increased. Maximum alteration of physical properties occurs from 8-10M zinc chloride, indicating maximum complex stability in this concentration range. The increased complexing is attributed to a reduction of the proportion of water as the zinc chloride concentration is increased (see page 17).

THE NATURE OF THE COMPLEX BETWEEN ZINC CHLORIDE AND THE CELLULOSE-RELATED COMPOUNDS

The term "complex" is used to describe a variety of types of interactions between molecules. It has a different significance for different investigators and is not subject to a brief all-encompassing definition. With this in mind, the observed properties of the complex with zinc chloride were considered and an attempt was made to select a model for the complex which best approximated these properties.

The properties of the aqueous zinc chloride complexes with cellulose-related compounds indicated that they would best be defined by considering them as molecular complexes in which the primary bonding forces were ion-dipole interactions. These molecular complexes are also referred to as charge transfer complexes. The zinc ions functioned as an electron acceptor and the model compound as an n-type electron donor. The n donors are ones in which there are nonbonded electrons (lone pairs) available. Typical examples of these n donors include alcohols, organic sulfides, organic iodides, and nitrogen bases, in which the lone pairs

of electrons are located, respectively, in atomic orbitals of oxygen, sulfur, iodine, and nitrogen atoms.

These electron donor-acceptor complexes, which can be represented by integral mole ratios of the components usually cannot be isolated in the pure state at ordinary temperatures, but exist only in solutions in equilibrium with their components. However, they can be detected by differences in their physical properties from those of the pure components. The rates of formation of complexes in solution are generally so rapid that kinetics studies by ordinary procedures are impossible. Heats of interactions are small and there is abundant evidence that the forces of coordination are much weaker than those established in the formation of covalent bonds. That is, the degree to which electron transfer takes place is much less than ordinarily occurs when new compounds are formed (29).

The observed physical properties of the complex between zinc chloride and the model compounds studied in this thesis almost exactly paralleled those of the molecular complexes described above. The observed changes in the physical properties (e.g., optical rotation and NMR chemical shift) took place in less than five minutes indicating rapid kinetics of complex formation. The continuous variations data indicated an integral mole ratio (1:1) of zinc chloride to model compound. Optical rotations deviations, changes in the NMR spectra, and deviation from expected ultraviolet absorbances supplied abundant evidence that electronic charge transfer occurred and the electronic distribution of the molecules involved was altered. Comparison of the deviations from expected behavior in the aqueous zinc chloride system to those observed for the ferric iron tartrate (19) and cuprammonium hydroxide systems (18), which were known to form strong complexes with cellulose-related model compounds, indicated that the interactions were weak in dilute zinc chloride solutions. However, complex stability increased markedly as the zinc chloride concentration was increased.

Although there has been extensive controversy over the description of the donor-acceptor type complex, the description of Milliken (30-32) is now generally accepted. Milliken describes a 1:1 donor-acceptor complex in the ground state N in terms of the wave function ψ_N.

$$\psi_N = a\,\psi_o\,(D,A) + b\,\psi_1(D^+\text{-}A^-) \qquad (8)$$

A loosely bound molecular complex (a>>b) is regarded as a resonance hybrid receiving major contribution from a no bond form and minor contribution from a dative form in which an electron has been transferred from the donor to the acceptor.

Consider the possible complex reaction between a hydrated zinc ion and a model compound, M. The law of mass action predicts

$$Zn(H_2O)_6^{++} + M \rightleftarrows Zn(H_2O)_4^{++}\cdots M + 2\,H_2O \qquad (9)$$

that the concentration of the complex would increase as the zinc chloride concentration is increased. This may account for the new infrared absorption maximum at 870 $cm.^{-1}$ (Table I) and the deviation from expected ultraviolet absorbance (Table III). However, the stability of the complex would also be expected to increase as the zinc chloride concentration is raised. This is an environmental effect due to the closer packing of molecules in the solution and the reduction of the water molecules available to hydrate the ions in solution. This is supported by the infrared frequency shifts (Table I) and by the increasing temperature dependence of the NMR chemical shift change (Table II). The concept of increased stability is also supported by the fact that the methyl ether group does not block complexing in concentrated solutions of zinc chloride.

LOCATION OF THE POINTS OF COMPLEXING ON THE GLUCOPYRANOSIDE RING

Location of the points of complexing was accomplished by a comparison of the behavior of partially and fully methylated glucopyranosides to that of the parent glucopyranosides. This was done by the method of continuous variations and with NMR spectra. The NMR spectra were measured for solutions containing equimolar amounts of zinc chloride and the model compound.

Due to the aqueous solubility limits of the model compounds no continuous variations experiments were performed at concentrations greater than 3.0M. The solvent effect for the ring protons of the glucopyranosides is negligible below 1.5M zinc chloride. This is supported by the fact that no change in $\Delta\nu$ with zinc chloride concentration is observed for the ring protons of methyl β-D-glucopyranoside at a constant molar ratio of salt to sugar (Table XVI).

BLOCKING OF COMPLEX FORMATION BY THE METHYL ETHER GROUP

The efficiency of the methyl ether group in blocking complex formation when it is substituted for an hydroxyl group can be ascertained from the behavior of three model compounds: methyl 2,3,4,6-tetra-O-methyl-β-D-glucopyranoside, hexa-O-methyl-myo-inositol, and ethyl 3,4,6-tri-O-methyl-β-D-glucopyranoside. Figure 1 illustrates that there was no complex formation between methyl 2,3,4,6-tetra-O-methyl-β-D-glucopyranoside and zinc chloride. In addition, no change in any of the chemical shifts (Appendix I) for these three compounds was observed in zinc chloride solutions (in D_2O) compared to their NMR spectra without zinc chloride, indicating no complexing. Lack of complex formation with ethyl 3,4,6-tri-O-methyl-β-D-glucopyranoside indicated that zinc chloride would not complex with a single hydroxyl or with a hydroxyl-methoxyl combination in a dilute aqueous solution of zinc chloride.

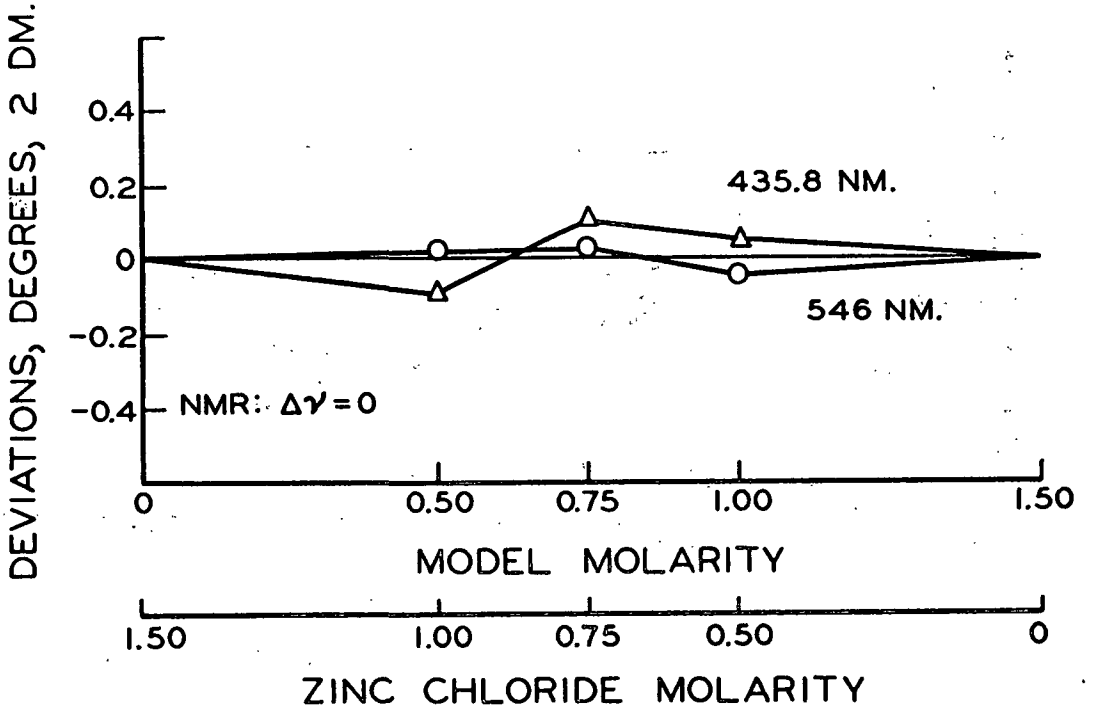


Figure 1. Optical Rotations Deviations: Zinc Chloride-Methyl 2,3,4,6-tetra-O-Methyl-β-D-glucopyranoside

DETERMINATION OF THE POINTS OF COMPLEXING

Since methylation of all the hydroxyl positions on the glucopyranoside ring completely blocked complex formation, and zinc chloride did not complex significantly with a single hydroxyl or a hydroxyl-methoxyl pair, it was concluded that a pair of hydroxyls must be involved.

Comparison of the deviation curves (Fig. 2 and 3) and the NMR chemical shift changes (Table IV) for methyl β-D-glucopyranoside and methyl 4,6-di-O-methyl-β-D-glucopyranoside* shows that the ability of the unsubstituted glucoside to complex with zinc chloride is altered little by the isolation of the glycol pair of hydroxyls on carbon atoms two and three as a result of the blocking of the remaining groups. Since monohydroxylic compounds do not complex, this vicinal hydroxyl pair must be the primary location on the sugar ring at which complex formation takes place.

*Only one point was possible in Fig. 3 due to a lack of this compound.

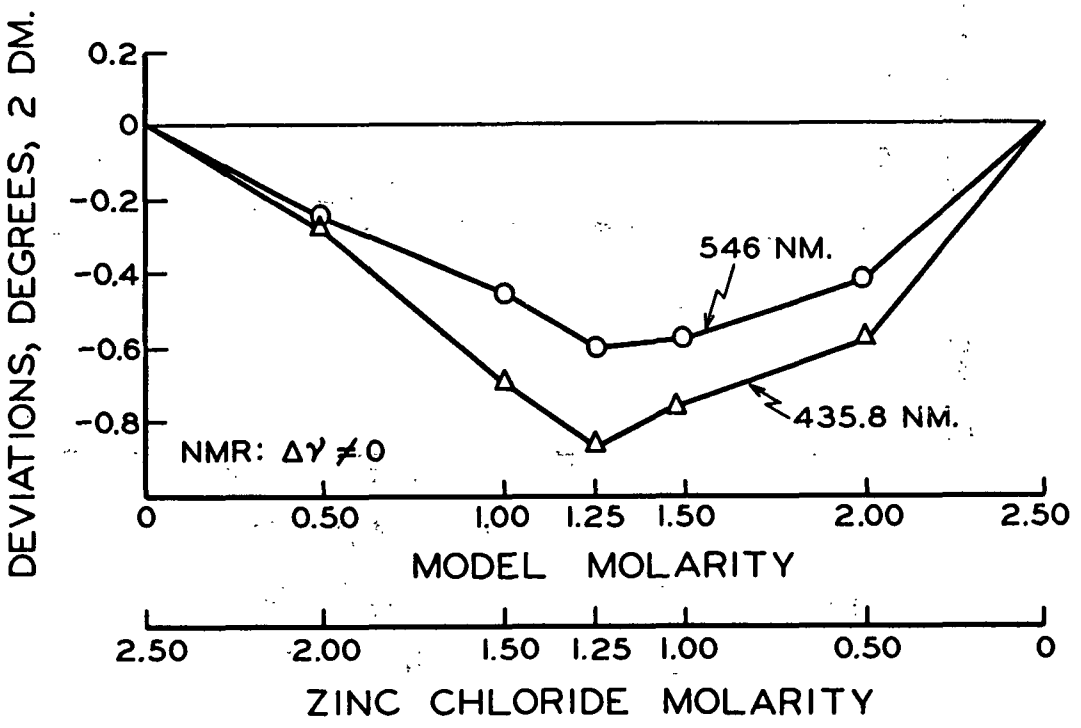


Figure 2. Optical Rotations Deviations: Zinc Chloride-Methyl β-D-Glucopyranoside

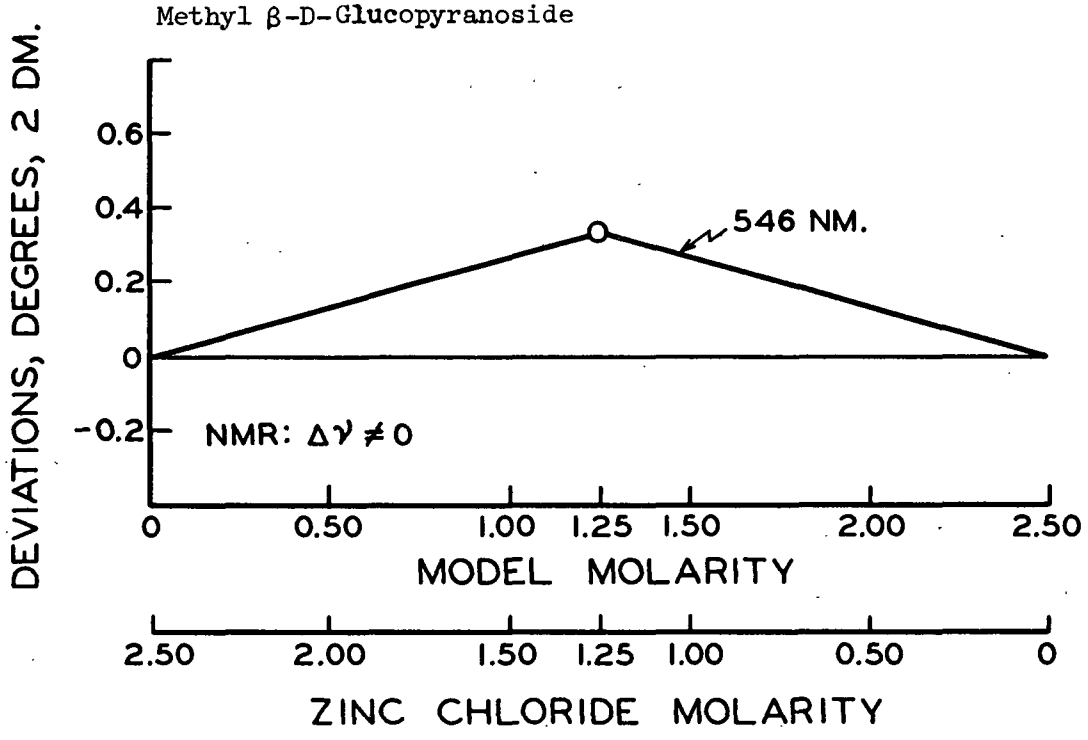


Figure 3. Optical Rotations Deviations: Zinc Chloride-Methyl 4,6-di-O-Methyl-β-D-glucopyranoside

TABLE IV

NMR RESULTS FOR METHYL β-D-GLUCOPYRANOSIDE AND METHYL 4,6-DI-O-METHYL-β-D-GLUCOPYRANOSIDE

Proton Peak Assignment	Chemical Shift Changes (Δν), c.p.s.
1.0M Methyl β-D-glucopyranoside + 1.0M $ZnCl_2$	
H_1 (anomeric protons)	2.05
$H_{2,3,4,5}$ (ring protons)	1.85
1.0M Methyl 4,6-di-O-Me-β-D-glucopyranoside + 1.0M $ZnCl_2$	
H_1	1.80
$H_{2,3,4,5}$	1.65

When the deviation curves (Fig. 4 and 5) and NMR data (Table V) for methyl α-D-glucopyranoside and methyl 3-O-methyl-(α,β)-D-glucopyranoside* (∿90% alpha) are compared, a sharp decrease in the tendency of the substituted glucoside to complex with zinc chloride is evident. This is a result of the absence of any vicinal diols due to the methoxyl group in position three. The slight residual complexing tendency of this model compound is attributed to a limited ability of the zinc chloride to complex with pairs of hydroxyls which are spaced further apart than a vicinal pair. This residual complex formation took place either at positions two and four on the ring or at positions four and six with that particular compound.

The behavior of the glucoside substituted at position three served as confirming evidence for the observed indication of complex formation between zinc chloride and the vicinal hydroxyls on the sugar ring. The unsubstituted glucopyranosides (both alpha and beta anomers) probably are capable of forming the complex involving hydroxyl groups at either two and three or positions three and four.

*Only one point was possible in Fig. 5 due to a lack of this compound.

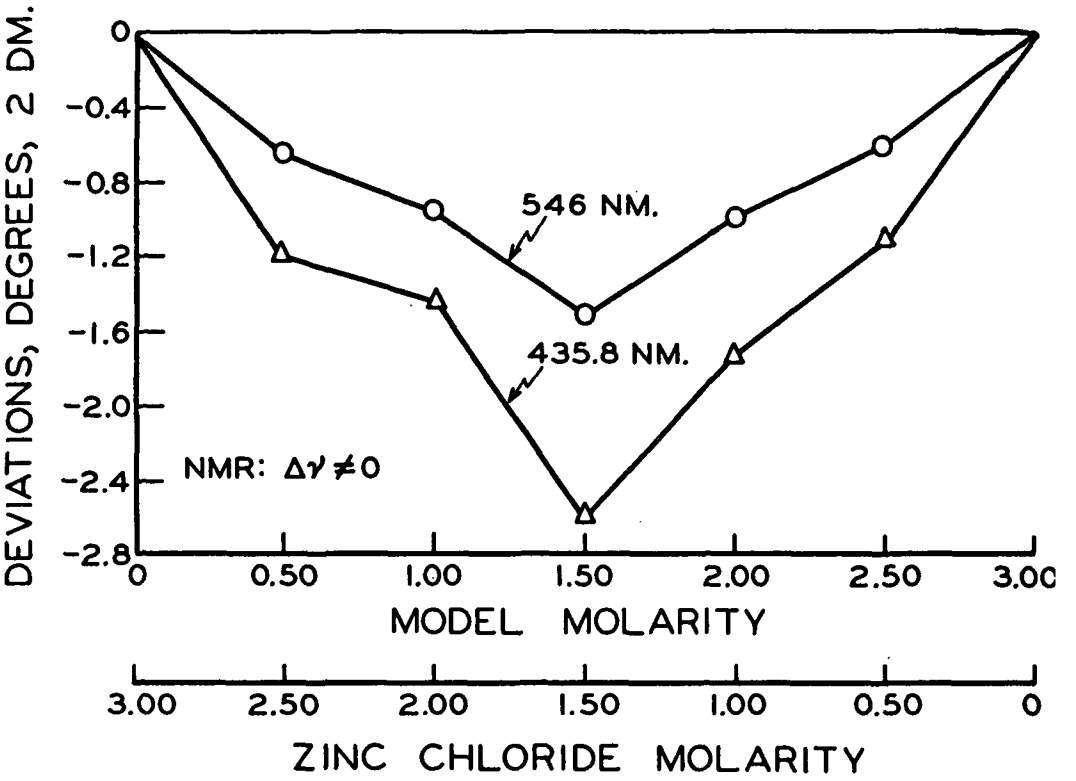


Figure 4. Optical Rotations Deviations: Zinc Chloride-Methyl α-D-Glucopyranoside

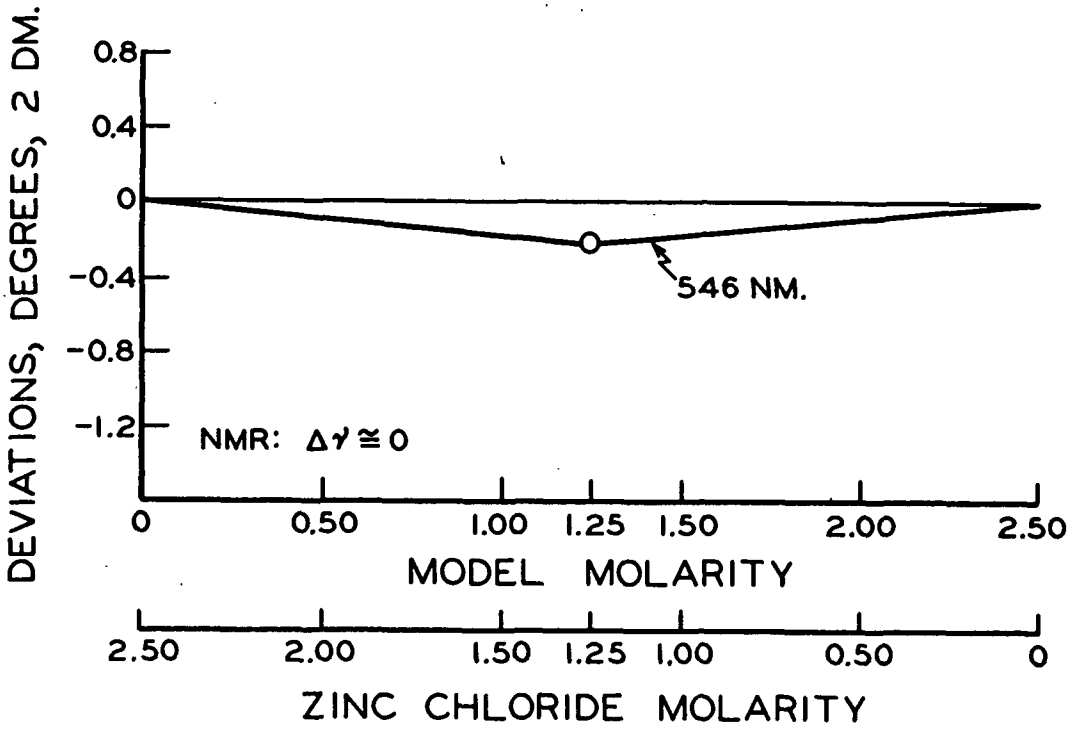


Figure 5. Optical Rotations Deviations: Zinc Chloride-Methyl 3-O-Methyl-(α,β)-D-glucopyranoside (∿90% Alpha Anomer)

TABLE V

NMR RESULTS FOR METHYL α-D-GLUCOPYRANOSIDE AND METHYL 3-O-METHYL (α,β)-D-GLUCOPYRANOSIDE (~90% ALPHA ANOMER)

Proton Peak Assignments	Chemical Shift Changes (Δν), c.p.s.
1.0M Methyl α-D-glucopyranoside + 1.0M $ZnCl_2$	
H_1 (anomeric proton)	1.30
$H_{2,3,4,5}$ (ring protons)	1.40
0.5M Methyl 3-O-methyl-(α,β)-D-glucopyranoside + 0.5M $ZnCl_2$	
H_1 (alpha anomeric proton)	0.10
H_1 (beta anomeric proton)	0.60
H_{OCH_3} (3-O-methyl protons)	0.00
H_{OCH_3} (beta glycosidic methoxyl protons)	0.10
H_{OCH_3} (alpha glycosidic methoxyl protons)	-0.25
$H_{2,3,4,5}$ (ring proton peaks)	
A	0.20
B	0.15

Although the location of the points of complexing was only determined for dilute solutions, the probable preferred points of complex formation at higher concentrations would be the same. The changes in the infrared spectra (ATR) exhibited by methyl 2,3,4,6-tetra-O-methyl β-D-glucopyranoside and hexa-O-methyl-myo-inositol in 9.5M zinc chloride solutions are attributed to complex formation; probably between two adjacent methoxyl ether groups. Under certain circumstances zinc chloride is known to form a crystalline complex with diethylene glycol dimethyl ether (33). This indicates that zinc chloride could complex with an ether linkage in concentrated solutions. Since the methoxyl group did not block complex formation in concentrated zinc chloride solutions, it was not possible to locate the points of complexing in concentrated solutions with the experimental methods used in this thesis.

COMPLEX FORMATION BETWEEN ZINC CHLORIDE AND OTHER MODEL COMPOUNDS

In addition to experiments with the methyl glucopyranosides, continuous variations deviation curves were obtained for methyl β-D-xylopyranoside and sorbitol (Fig. 6 and 7), and NMR chemical shifts were measured for methyl 6-deoxy-β-D-glucopyranoside, methyl β-D-xylopyranoside, myo-inositol, sorbitol, glycerol, ethylene glycol, methyl cellosolve, ethanol, and n-propanol (Tables VI-VIII).

The NMR chemical shift changes ($\Delta\nu$) for ethylene glycol, methyl cellosolve, and ethanol in aqueous zinc chloride solutions (Table VIII) indicated the presence of a solvent effect for these molecules. That is, the chemical shifts exhibited changes which were dependent on the polarity of the solution. Chemical shift measurements for methyl β-D-xylopyranoside also exhibited small solvent effects. The solvent effect for the other model compounds was found to be negligible (experimental data, Appendix I).

Inspection of the continuous variations and NMR data indicates that the model compounds which possessed one or more vicinal pairs of hydroxyls, and at least one extra oxygen not involved in the complex, exhibited complex formation with aqueous zinc chloride. If the NMR solvent effect is considered, there is little or no complex formation with ethylene glycol, methyl cellosolve, and ethanol. While no solvent effect was evident, the NMR chemical shifts of n-propanol did not change in the presence of zinc chloride indicating no complexing. Thus, those compounds which contain no vicinal hydroxyls or vicinal hydroxyls and no extra oxygens exhibit little or no complexing.

The necessity of additional oxygen atoms was probably related to the solubility effect of these electronegative groups in an aqueous medium (34). For example, the zinc derivative of 8-hydroxy-quinoline is quantitatively insoluble in water,

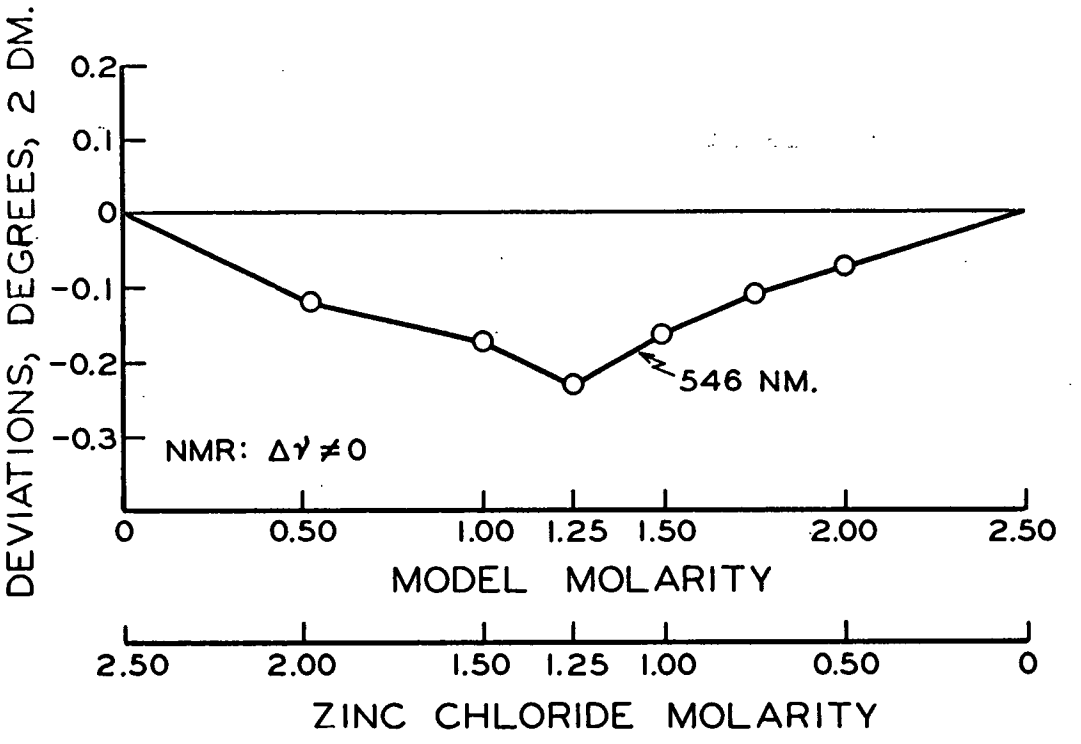


Figure 6. Optical Rotations Deviations: Zinc Chloride-Methyl β-D-Xylopyranoside

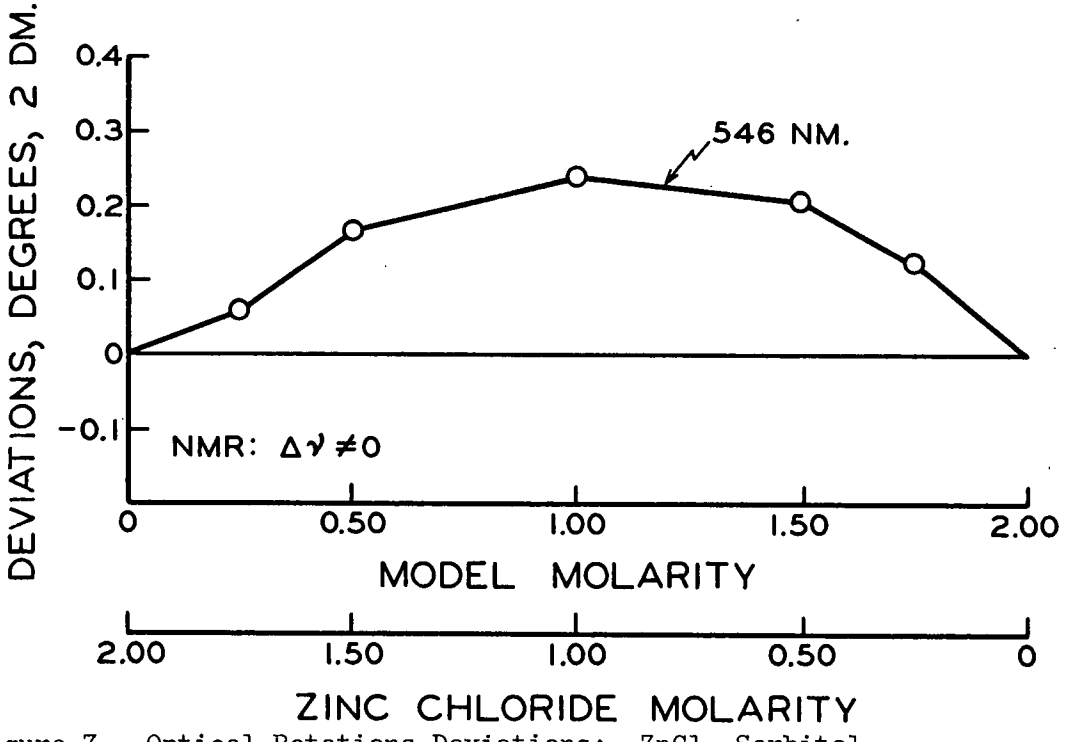


Figure 7. Optical Rotations Deviations: $ZnCl_2$-Sorbitol

TABLE VI

NMR RESULTS FOR METHYL 6-DEOXY-β-D-GLUCOPYRANOSIDE AND METHYL β-D-XYLOPYRANOSIDE

Proton Peak Assignments	Chemical Shift Changes ($\Delta\nu$), c.p.s.
1.0M Methyl 6-deoxy-β-D-glucopyranoside + 1.0M $ZnCl_2$	
H_1 (anomeric proton)	2.30
$H_{2,3,4,5}$ (ring proton peaks)	
A	1.95
B	0.95
C	1.65
D	1.15
0.5M Methyl β-D-xylopyranoside + 0.5M $ZnCl_2$	
H_1	1.65
$H_{2,3,4,5}$	
A	0.90
B	1.30
C	0.95
D	1.25
E	1.90
F	1.40
G	1.40

TABLE VII

NMR RESULTS FOR MYO-INOSITOL, SORBITOL, AND GLYCEROL

Proton Peak Assignments	Chemical Shift Changes ($\Delta\nu$), c.p.s.
0.5M myo-Inositol + 0.5M $ZnCl_2$	
Ring proton peaks	
A	1.00
B	0.75
C	0.95
D	1.15
E	1.55
F	1.35
0.5M Sorbitol + 0.5M $ZnCl_2$	
Chain proton peaks	
A	2.05
B	2.15
C	1.65
0.5M Glycerol + 0.5M $ZnCl_2$	
Main peak of spectrum	1.90

TABLE VIII

NMR RESULTS FOR ETHYLENE GLYCOL, METHYL CELLOSOLVE, ETHANOL, AND n-PROPANOL

Proton Peak Assignments	Control (no $ZnCl_2$)	Chemical Shift, Changes ($\Delta\nu$), c.p.s. 0.5M Model +0.5M $ZnCl_2$	1.5M Model +1.5M $ZnCl_2$
Ethylene glycol			
H_{CH_2OD}	0.00	0.70	1.30
Methyl cellosolve			
H_{CH_2OD}	0.00	0.70	1.30
H_{CH_2}	0.00	0.75	1.05
H_{CH_3}	0.00	-0.15	0.30
Ethanol			
H_{CH_2OD}	0.00	0.95	1.20
H_{CH_3}	0.00	0.30	0.75
n-Propanol			
H_{CH_2OD}	0.00	-0.40	0.00
H_{CH_2}	0.00	-0.25	-0.15
H_{CH_3}	0.00	0.15	0.05

whereas the zinc compound of 5-sulfo-8-hydroxyquinoline is readily soluble. The aqueous insolubility of a complex with a compound containing only a glycol group and no extra oxygens might cause a change in the equilibrium in aqueous solutions, which would reduce, if not eliminate, complex formation. This is the probable explanation for the little or no complexing observed with ethylene glycol.

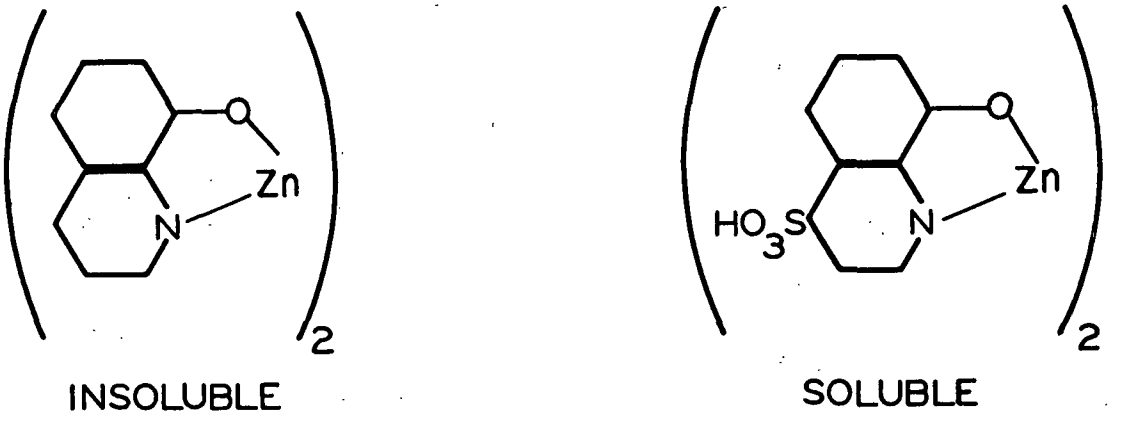


Figure 8. Effect of Extra Electrophilic Groups on the Solubility of a Zinc Complex

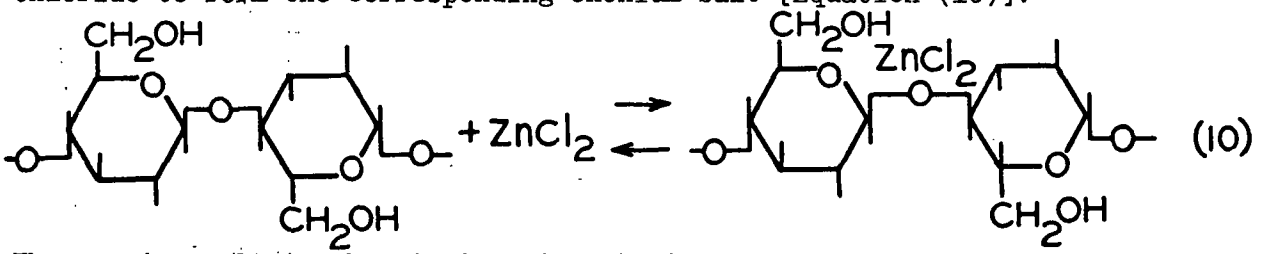
POSSIBLE CELLULOSE SWELLING MECHANISM

Various theories, both chemical and physical, have been proposed to account for the observed phenomena which occur when cellulose is contacted with zinc chloride. None of these theories has been adequate and much disagreement has existed as to their status. Kasbekar (35-37) has comprehensively reviewed these theories and discussed in detail the three most credible ones; the osmotic theory of swelling, physical adsorption of the solute, and compound formation of the oxonium type.

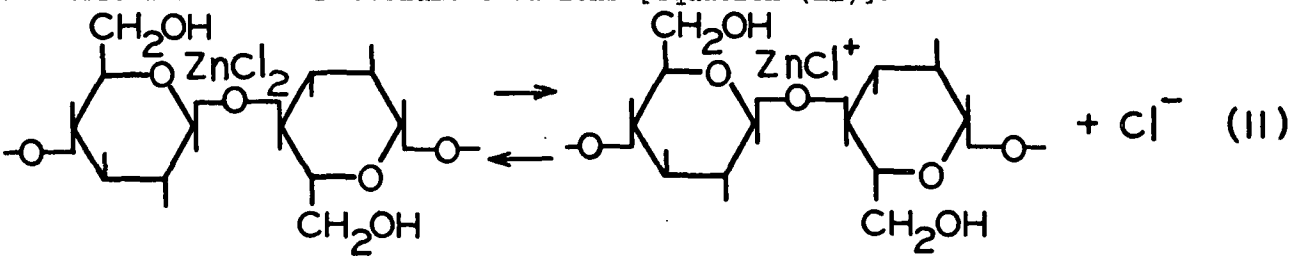
The osmotic theory requires the formation of compounds of cellulose with the swelling agent, their solution in the swelling medium inside the gel phase,

and consequent development of osmotic pressure due to unequal distribution of the dissolved compound on either side of an imaginary membrane which separates the gel from the swelling medium. This theory has been rejected by Kasbekar (36) on the basis of incompatibility with experimental fact (36). Kasbekar (35) also rejects the physical adsorption theory because it would probably not account for the large changes in swelling.

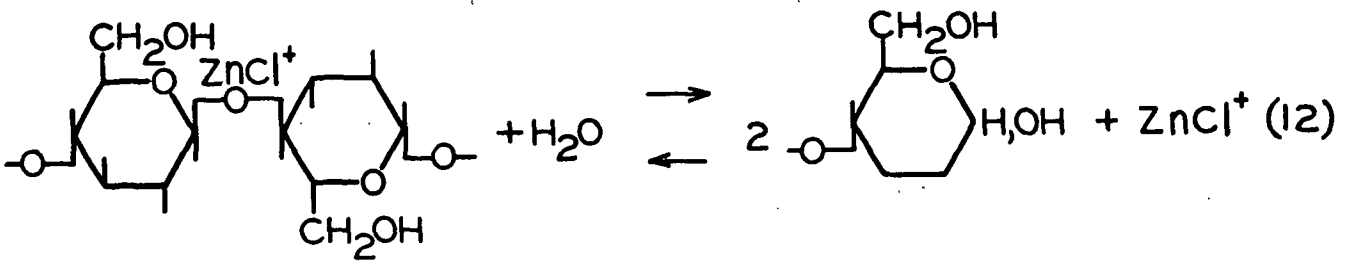
Kasbekar (36) favors the theory of oxonium salt formation to explain the swelling and dissolving of cellulose which is treated with zinc chloride solutions. According to this theory, cellulose molecules combine with zinc chloride to form the corresponding oxonium salt [Equation (10)].



The oxonium salt is then ionized in solution to give diffusible anions and nondiffusible oxonium cellulose cations [Equation (11)].



The cation may then react with water to form hydrocellulose by cleaving the glycosidic linkage [Equation (12)].



Kasbekar's theory has been the most credible one advanced prior to this thesis. However, it is incorrect on several basic points. Complex formation does not take place at the glycosidic linkage. This thesis has demonstrated that complex formation between zinc chloride and cellulose is probably a chelate structure with zinc coordinating with the oxygens of hydroxyl positions two and three on the glucopyranoside ring. In general, studies of complex formation with carbohydrates have shown no indication that the oxygen of the glycosidic linkage can participate (14,19). In addition, Raman studies (11) have shown that $ZnCl^{+}$(aq.) exists in only very small amounts in solutions less than 4M whereas gelatinization of cellulose occurs from about 8-10M. Also, the evidence presented in the following section indicates that hydrolysis takes place by way of the normal proton catalyzed hydrolysis mechanism.

A number of parallels between complex formation with cellulose-related model compounds and the actual cellulose swelling and crystallinity behavior have been observed. Based on these observed parallels, the following theory for the swelling and solution of cellulose in aqueous zinc chloride solutions is proposed.

Complex formation takes place through a chelate structure with a zinc ion [probably Zn^{++}(aq.)] coordinating with the oxygens of hydroxyl positions two and three of the glucopyranoside ring. This complex formation would disrupt the hydrogen-bonded crystalline structure of the cellulose and allow swelling to occur.

In support of this theory, the parallels between complex formation with cellulose-related model compounds and the swelling and crystallinity behavior of cellulose are discussed below.

Table IX and Fig. 9 illustrate the swelling (3) and crystallinity (4) of cellulose in zinc chloride solutions. Table X presents a comparison of the actual

TABLE IX

EFFECT OF THE ZINC CHLORIDE CONCENTRATION ON THE SWELLING OF COTTON CELLULOSE (3)

$ZnCl_2$, % (weight basis)	Swelling, % increase on dry weight
10.53	108.3
20.51	140.0
20.97	166
40.81	223
54.8	535
55.6	872
57.2	1,090
58.7	1,764
60.6	2,430
61.6	5,955
62.8	7,340
63.6	9,035
64.7	10,000
67.4	13,000
68.3	12,500
68.9	13,000
71.0	12,600
73.0	13,000

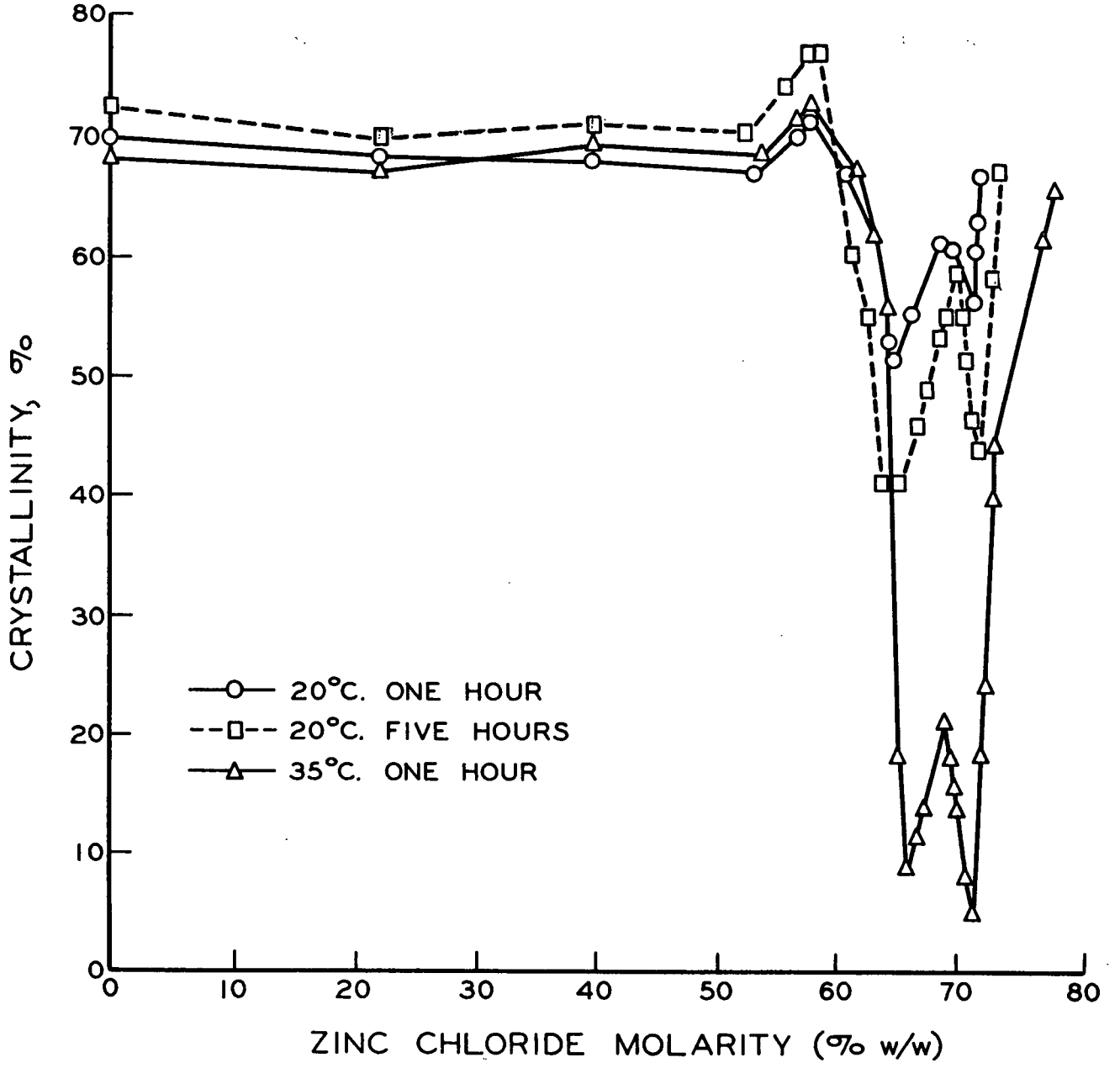


Figure 9. Decrystallization of Cotton by Zinc Chloride (4)

TABLE X

HYDRATION REQUIREMENTS OF THE AQUEOUS ZINC CHLORIDE SYSTEM

Stoichiometric Zinc Chloride Concentration,		$ZnCl_4(H_2O)_2^{--}$ Molarity (11)	$Zn(H_2O)_6^{++}$ Molarity (11)	Hydration Requirements (Mole Ratio) (H_2O/Zn)	
Wt. %	Molarity			Actual	Required
10	0.80	--	0.80	68.50	6.00
20	1.74	0.20	1.54	30.20	5.55
30	2.84	0.90	1.94	17.60	4.75
40	4.16	1.90	2.26	11.35	4.16
50	5.75	2.20	3.55	7.58	4.50
52	6.12	2.40	3.72	7.00	4.44
54	6.50	2.50	4.00	6.45	4.45
56	6.89	2.60	4.29	5.95	4.55
58	7.28	2.65	4.63	5.50	4.55
60	7.70	2.70	5.00	5.05	4.60
62	8.20	2.80	5.40	4.65	4.64
64	8.64	2.80	5.84	4.25	4.70
66	9.10	2.80	6.30	3.90	4.78
68	9.60	2.80	6.80	3.57	4.83
70	10.07	2.80	7.27	3.24	4.92
72	10.65	--	--	2.96	--
74	11.20	--	--	2.66	--
76	11.80	--	--	2.38	--
78	12.45	--	--	2.14	--
80	13.05	--	--	1.89	--

and the estimated required ratio of water to zinc. The values for the required water-to-zinc ratio were calculated for $Zn(H_2O)_6^{++}$ and $ZnCl_4(H_2O)_2^{--}$; the presence of $ZnCl^+$(aq.), and Cl^- was assumed to be negligible. Therefore, the actual hydration requirements will be slightly higher (sample calculations, Appendix IV).

Comparison of the effect of zinc chloride concentration on complexing with model compounds (Tables I-III) and the swelling and crystallinity loss of cellulose (Table IX and Fig. 9) illustrate that they closely parallel each other.

In addition, it has been observed that the hot (55-60°C.) vulcanization process does not produce as good quality product as the cold one (25-35°C.) (38). The effect of temperature on the NMR chemical shift changes ($\Delta\nu$) of methyl β-D-glucopyranoside (Table II) has demonstrated that $\Delta\nu$ is reduced by increasing the temperature (in the 8-10M range), indicating a reduction in complexing. Since the swelling of cellulose at about 9-10M is the basis of the vulcanization process, this would be expected assuming that complex formation plays a role in the swelling process.

These parallels are interpreted to mean that complex formation of a similar nature to that observed for cellulose-related model compounds is probably responsible for the behavior of cellulose in zinc chloride solutions.

The hydration requirements of zinc chloride in Table X illustrate how complexing would be expected to increase as the zinc chloride concentration is increased. As the amount of water is reduced, the zinc chloride will complex more with the model compound (or with cellulose). The increase in complexing would be small until the actual water available is insufficient to hydrate the zinc chloride ions. At this point (∿8M) the lack of water would create a ligand deficiency relative to the zinc ions in solution. This ligand deficiency would be satisfied by

a pair of glycol groups on a model compound or on the cellulose chain, and would account for the marked increase in complexing with model compounds and the swelling and crystallinity loss observed for cellulose in the 8-11M range.

As the zinc chloride concentration is increased, the water shortage becomes more severe and zinc chloride begins to selfassociate to form a polymeric aggregate at about 10M. Eventually, formation of this polymeric species with the attendant viscosity increase becomes so extensive (~11.5M) that the cellulose swelling and crystallinity changes approach values essentially the same as in dilute solutions.

SUPPLEMENTARY EXPERIMENTAL RESULTS

HYDROLYSIS OF THE GLYCOSIDIC BOND IN CONCENTRATED SALT SOLUTIONS

Hydrolysis rates for methyl β-D-glucopyranoside in 1.0N hydrochloric acid and varying concentrations of zinc chloride and lithium chloride at room temperature (26°C.) illustrate that acidic hydrolysis of the glycosidic linkage was accelerated in these concentrated salt solutions (Table XI). This acceleration of the glycosidic hydrolysis was also observed for methyl 2,3,4,6-tetra-O-methyl-β-D-glucopyranoside, methyl α-D-glucopyranoside, methyl β-D-xylopyranoside, and methyl 6-deoxy-β-D-glucopyranoside. The relative rates of hydrolysis for these carbohydrates were the same as in ordinary acid hydrolysis. Also, it was observed that the addition of LiCl, $Zn(ClO_4)_2 \cdot 6H_2O$ or $NaClO_4$ to zinc chloride solutions containing methyl β-D-glucopyranoside and hydrochloric acid accelerated the glycosidic hydrolysis relative to the same solution without the extra salt addition.

Verification of the optical rotation change as due to hydrolysis was accomplished by NMR spectra and analysis for methanol by the method of Boos modified by Robins (39). With time the hydrolyzed pyranosides developed a dark brown color in concentrated zinc chloride solutions.

TABLE XI

EFFECT OF THE SALT CONCENTRATION ON THE RATE OF HYDROLYSIS OF THE GLYCOSIDIC LINKAGE

Salt Concentration, molarity	Changes in the Observed Optical Rotation, $(\alpha)^{26}_{546}$, degrees Elapsed Time		
	5 Hours	10 Hours	15 Hours
0.5M Methyl β-D-glucopyranoside + 1.0N HCl + $ZnCl_2$			
3.0	0.00	0.00	0.01
4.0	0.00	0.00	0.02
5.0	0.20	0.30	0.35
6.0	0.80	1.00	1.10
6.5	1.00	2.50	3.20
7.0	1.25	3.10	3.90
7.5	2.50	3.90	5.60
8.0	8.90	13.00	15.30
8.5	9.30	13.60	15.50
9.0	11.50	16.10	17.80
9.5	13.40	17.00	19.00
0.25M Methyl β-D-glucopyranoside + 1.0N HCl + LiCl			
	3 Hours		18 Hours
10.0	1.60		7.20
12.0	7.90		15.20

Since acceleration of the acid hydrolysis of the glycosidic linkage occurred in lithium chloride as well as zinc chloride solutions, it was concluded that this phenomenon is due to the polar nature of the solutions. The acceleration of reactions having a polar intermediate in polar solvents is well known (40). The carbonium ion intermediate of the glycosidic hydrolysis is an example of such an intermediate.

Most workers have reported a drop in the D.P. of cellulose in concentrated zinc chloride solutions; however, the magnitude of the change in D.P. has varied widely. Since no hydrolysis of methyl β-D-glucopyranoside occurred at any zinc chloride concentration from 0-11.5M without the addition of hydrochloric acid, it was concluded that the reported changes in the D.P. of cellulose observed at moderate temperatures (~25-70°C.) are probably due to the addition of hydrochloric acid to adjust the basicity of the zinc chloride solutions. Hydrolysis would then be accelerated in the same way as for the pyranosides. The hydrolysis and decomposition of cellulose in concentrated zinc chloride solutions at elevated temperatures in the absence of hydrochloric acid is attributed to localized proton concentrations created by the ionization of water by zinc chloride according to the following reaction (41).

$$Zn(H_2O)_6^{++} \rightleftharpoons Zn(H_2O)_5^{++}\cdots OH^{-}\cdots H^{+} \qquad (13)$$

COMPLEX FORMATION WITH OTHER NEUTRAL SALTS

The NMR results presented in Table XII illustrate that there are changes in the chemical shifts of the peaks representing the anomeric (H_1) and the other ring protons ($H_{2,3,4,5}$) of methyl β-D-glucopyranoside in aqueous solutions of NaCl, LiCl, $Zn(ClO_4)_2 \cdot 6H_2O$, $ZnSO_4 \cdot 7H_2O$, or $CaCl_2 \cdot 2H_2O$. From a comparison of the chemical shift changes in Table XII, it is evident that the chemical shift changes are smaller for the other neutral salts than for zinc chloride. This infers that methyl β-D-glucopyranoside may complex with these salts, but the complexes formed are less stable than with zinc chloride.

TABLE XII

NMR RESULTS FOR METHYL β-D-GLUCOPYRANOSIDE[a] IN VARIOUS SALT SOLUTIONS

	Chemical Shift Changes (Δν), c.p.s.					
Proton Peak Assignments	0.5M LiCl	0.5M NaCl	0.5M $ZnSO_4 \cdot 7H_2O$	0.5M $Zn(ClO_4)_2 \cdot 6H_2O$	0.5M $CaCl_2 \cdot 2H_2O$	0.5M $ZnCl_2$
H_1	0.40	0.45	1.10	1.00	0.85	2.05
$H_{2,3,4,5}$	0.30	0.25	0.95	0.90	0.50	1.85

[a]The methyl β-D-glucopyranoside concentration was 0.5M.

EXPERIMENTAL PROCEDURES AND TECHNIQUES

Unless otherwise specified, all chemicals used were reagent grade and were weighed with the indicated accuracy. Details for the preparation of all model compounds are given in Appendix II. All solutions were made with triply distilled water, which was prepared by a second distillation of ordinary distilled water from an alkaline permanganate solution, followed by a third distillation in which the water had been acidified with a few drops of sulfuric acid. Both distillations were from an all-glass apparatus.

PREPARATION AND ANALYSIS OF STANDARD ZINC CHLORIDE SOLUTIONS

Standard zinc chloride solutions were prepared using Fisher reagent-grade chemical without further purification. Although some zinc carbonate precipitation occurred on exposure to air, regular checks throughout their period of use showed no significant change in the concentrations of these standard solutions. With the exception of the deuterated solutions used in NMR work, solutions containing zinc chloride were prepared by dilution of these standard solutions.

Preparation of the standard zinc chloride solutions was accomplished by weighing (to the nearest 0.1 g.) the amounts of zinc chloride and water calculated for an approximate desired concentration into a beaker. The mixture in the beaker was heated at about 60°C. until complete solution occurred, and then transferred to a volumetric flask and sealed with a ground glass stopper.

Initially, the exact concentration of zinc chloride was determined by two methods; specific gravity, and a titrimetric method. When it was discovered that the specific gravity and titrimetric method gave the same results, the more complicated and time consuming titrimetric method was abandoned in favor of the simpler specific gravity method. Table XIII illustrates a comparison of the two methods.

TABLE XIII

DETERMINATION OF THE ZINC CHLORIDE CONCENTRATION BY SPECIFIC GRAVITY AND TITRIMETRIC METHODS

Zinc Chloride (Calc.), %	Temperature, °C.	Density, g./ml.	Zinc Chloride, molarity: Sp. Gr. Method	Zinc Chloride, molarity: Titration Method
33.90	24.0	1.336	3.31	3.36
54.44	22.5	1.643	6.56	6.53
72.65	22.5	2.023	10.78	10.82
78.11	22.5	2.166	12.41	12.41

The specific gravity was determined by weighing twenty-five milliliters of the standard zinc chloride solution to the nearest 0.1 mg. in a sealed twenty-five milliliter volumetric flask at room temperature. The concentration of the solution was obtained from a table of specific gravity versus zinc chloride concentration as a function of temperature (42). All determinations were in duplicate.

The titrimetric method was a slight modification of the method of Shalfeev and Dobrovol'skaya (43) for the simultaneous determination of zinc and ammonia ions in solutions of zinc and ammonium chloride by titration with sodium hydroxide.

Briefly, the titrimetric method was as follows. To twenty milliliters of approximately 0.1N zinc chloride, three to five drops of 0.1% methyl red and one drop of 0.05% methylene blue indicators were added; the solution was then green. This solution was neutralized with 0.1N hydrochloric acid to a violet end point. Four to five drops of 0.1% phenolyphthalein indicator were added and the solution was titrated with 0.1N sodium hydroxide to a yellow-brown end point, adding about one to two milliliters of sodium hydroxide per minute.

CONTINUOUS VARIATIONS METHOD

In essence, the continuous variations method employs the measurement of some property of a solution as a function of the molar ratio of the reacting species. Total molarity of the reacting species is constant. A maximum or minimum occurs at the molar ratio corresponding to the composition of the complex. The change in the property of the solution is more evident, if the difference between the experimental value and the value calculated assuming no complex formation is plotted as a function of the initial molar ratio of the reacting species. The mathematics of this method have been developed in detail by several workers and will not be repeated here (44-47).

Jones and Innes (46) have discussed the various physical properties that are suitable for the method of continuous variations. These properties are classified as those characteristic of the ions or molecules themselves, and those, while characteristic of the solution, can be apportioned to the various species in solution on the basis of their concentration. Properties such as light absorption, optical rotation, and NMR are in the first category, while factors such as refraction are in the latter category.

Both optical rotation and refractive index measurements were applied to the method of continuous variations in this study. The refractive index measurements of mixtures of zinc chloride and model compound exhibit a solvent effect which appears to be unrelated to complex formation, and dependent only on the solution properties. Therefore, the refractive index data are presented in Appendix I, and not in the results.

PREPARATION OF THE SOLUTIONS FOR THE METHOD OF CONTINUOUS VARIATIONS

The continuous variation method requires the establishment of a constant total molarity. That is, the sum of the molarities of zinc chloride plus the model compound equals a constant. Due to aqueous solubility limits for the model compounds several total molarities were used. These were: 3.0M methyl α-D-glucopyranoside, 2.5M methyl β-D-glucopyranoside, methyl 4,6,-di-O-methyl-β-D-glucopyranoside, methyl 3-O-methyl-(α,β)-D-glucopyranoside, and methyl β-D-xylopyranoside; 2.0M sorbitol; 1.5M methyl 2,3,4,6-tetra-O-methyl-β-D-glucopyranoside; 0.9M mannitol.

With the exception of methyl 4,6-di-O-methyl-β-D-glucopyranoside and methyl 3-O-methyl-(α,β)-D-glucopyranoside, the following method was used to prepare the solutions of zinc chloride and model compound for the continuous variations optical rotations and refractive index measurements. All determinations were at least duplicate and all weighings were to the nearest 0.1 mg.

The amount of model compound corresponding to the desired molarity was weighed in a ten or twenty-five milliliter volumetric flask, and dissolved in a minimum of water. The amount of standard zinc chloride solution corresponding to the desired molarity was pipetted into the volumetric flask and a single drop of fifteen percent hydrochloric acid was added to disperse any zinc oxychloride floc. The contents of the volumetric flask were then diluted to volume at equilibrium in a 20°C. water bath. Pure component solutions were prepared by adding the calculated amount of model compound or standard zinc chloride solution to a volumetric flask and diluting to volume. All solutions remained clear and transparent even after storage at room temperature (20-27°C.) for several months.

The optical rotation of each solution was measured to 0.01° with a Zeiss-Winkel polarimeter. An average of at least ten readings for solution and zero was obtained. Optical rotations measurements were made at 546 and 435.8 nm. with a filtered mercury light source. For methyl α- and β-D-glucopyranosides a constant temperature bath (20 ± 0.02°C.) was used in conjunction with a two-decimeter, jacketed polarimeter tube. All other compounds were measured with a two-decimeter polarimeter tube at room temperature (24-28°C.).

The procedure for methyl 4,6-di-O-methyl-β-D-glucopyranoside and methyl 3-O-methyl-(α,β)-D-glucopyranoside was essentially the same as above with the following modifications.

A specially prepared volumetric flask (one milliliter) made from an eye-dropper and calibrated with a one milliliter pipet at 20°C. was used. Instead of pipetting the zinc chloride into the volumetric flask, the calculated amount of Fisher's reagent zinc chloride, corrected for impurities and water content, was weighed into the volumetric flask containing the model compound, and approximately 0.005 ml. of fifteen percent hydrochloric acid was added. The solution was then diluted to volume at equilibrium with a 20°C. water bath. Optical rotation measurements were made at 546 nm. with a microbore, two-decimeter polarimeter tube. An average of at least twenty-five readings for sample and zero was obtained.

Refractive index measurements were made at 20 ± 0.1°C. with a Bausch and Lomb Abbé refractometer for solutions of methyl α- and β-D-glucopyranosides, methyl 2,3,4,6-tetra-O-methyl-β-D-glucopyranoside, glycerol, ethylene glycol, ethanol, and methanol. These continuous variations data are reported in Appendix I.

NMR SPECTRA

A complete discussion of the theory and use of NMR is provided by Emsley, et al. (25).

All NMR spectra were obtained for deuterated solutions using a Varian Model A-60A analytical NMR spectrometer operating at a frequency of 60 MH. The chemical shifts of these spectra were measured for solutions in 99.8% deuterium oxide (Stohler Isotope Company) containing 3-(trimethylsilyl)-propane sulfonic acid sodium salt (DSS) as an internal reference.

All weighings were to the nearest 0.1 mg., and all chemical shifts reported in this thesis were an average of five or more identical spectra for each deuterated solution.

The deuterated solutions of model compound and zinc chloride were prepared by weighing the amount of model compound and Fisher's reagent zinc chloride corresponding to the desired molarity into the quart glass coaxial sample tube used for NMR measurements. Following this, a small amount of DSS in D_2O and approximately 0.001 ml. of concentrated hydrochloric acid were added, and the contents of the sample tube were diluted to a height of five centimeters which corresponded to a volume of 0.434 ml.

INFRARED SPECTRA

All infrared data (3000-800 $cm.^{-1}$) were obtained by the method of attenuated total reflectance (ATR) using a silver chloride prism in a Perkin-Elmer model 21 recording spectrometer. Basically, the reflectance spectra are the same as normal transmission spectra, but instead of transmitting a beam through the sample, the beam is multiply reflected from the surface of the sample. The principal advantage of this method is that it reduces the amount of absorption of

energy by the solvent; thus, it is feasible to obtain infrared spectra of aqueous solutions. A complete discussion of the theory of the ATR method is provided by Fahrenfort (48) and Hansen (49).

The aqueous solutions of model compound and zinc chloride were prepared by weighing the amount of model compound and standard zinc chloride solution, corresponding to the desired molarity into a twenty-five milliliter volumetric flask, and diluting the contents to volume at equilibrium with a 20°C. water bath. For solutions less than 3M in zinc chloride, it was necessary to add a drop of fifteen percent hydrochloric acid in order to disperse any zinc oxychloride floc. Above 3M no floc formation occurred.

ULTRAVIOLET SPECTRA

The ultraviolet spectra were obtained using a one or ten centimeter silica glass cell in a Cary model 15 recording spectrophotometer. Solutions were prepared in the same manner as for the infrared spectra.

HYDROLYSIS RATES

Solutions of glycopyranoside and zinc chloride in 1.0N hydrochloric acid were prepared by weighing the desired amount of glycopyranoside into a tared aluminum dish and dissolving it in a minimum of water. The desired amount of standard zinc chloride solution and concentrated hydrochloric acid were then weighed into a twenty-five milliliter volumetric flask. Initial reaction time was recorded when the glycopyranoside and the contents of the volumetric flask were mixed, and diluted to volume at equilibrium with a 20°C. water bath. Following this, the mixture was transferred to a two-decimeter polarimeter tube and the optical rotation at 546 nm. was followed as a function of time from initial reaction. Hydrolysis rates were always obtained relative to a control at the same temperature.

CONCLUSIONS

In dilute aqueous solutions, those compounds which contain a contiguous glycol group and extra oxygens complex well with zinc chloride, but those which contain a glycol group and no additional oxygens or contain no glycol group exhibit little or no complex formation. Consideration of the properties of these complexes indicates that they would probably best be classed as molecular complexes in which the primary forces of attraction are ion-dipole interactions. The methyl ether group blocks this reaction in dilute zinc chloride solutions but not in concentrated ones. The points of complexing on the glucopyranoside ring are the glycol pairs of hydroxyls at positions two and three and three and four.

Although the forces of interaction are weak in dilute solutions, complex stability increases as the zinc chloride concentration is raised. The maximum increase in complexing occurs in the 8-10M range. In this concentration range there is insufficient water to hydrate the zinc ions, which accounts for the maximum increase in complexing in this range.

Parallels between the complex formation with cellulose-related model compounds and the actual cellulose swelling and crystallinity behavior indicate that the formation of a complex between cellulose and zinc chloride is probably involved in the swelling mechanism.

Acidic hydrolysis of the glycosidic linkage is accelerated in concentrated aqueous solutions of zinc chloride at room temperature. No hydrolysis occurs at any zinc chloride concentration without the addition of hydrochloric acid.

SUGGESTIONS FOR FUTURE WORK

Further studies of aqueous zinc chloride as a cellulose swelling agent should be directed toward isolation of crystalline complexes (if possible) and studies of the nature of the coordination between zinc chloride and cellulose-related compounds. These studies would probably be best conducted for concentrated solutions because complex stability is greater there than at dilute concentrations.

Attempts to obtain more direct evidence of complex formation between zinc chloride and cellulose from infrared spectra of aqueous mixtures of cellulose and $ZnCl_2$ were unsuccessful. The samples were not transparent enough for transmission spectra, and reflectance spectra (ATR) failed because sufficient contact between the cellulose and the prism was not obtained. If these difficulties could be overcome, useful results could probably be obtained.

It has been observed that concentrated salt solutions accelerate hydrolysis of the glycosidic linkage and that a dark brown color develops with time as a result of the degradation of the carbohydrate following hydrolysis. Since it is conceivable that a high, local concentration of salt exists in a sheet or roll of paper stored at low relative humidity, if there were any free protons available they could cause local hydrolysis followed by a color change which might be responsible for brightness reversion of paper in storage.

Studies of this phenomenon might be conducted by examining the relationship of brightness reversion to the ash content and relative humidity of storage of the paper.

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APPENDIX I

EXPERIMENTAL DATA

TABLE XIV

CONTINUOUS VARIATIONS DATA

Optical Rotation (degrees, two decimeters)

Zinc Chloride-Model Compounds

1. Methyl α-D-glucopyranoside (20°C.)

Molarity $ZnCl_2$/Model	Model Rotation 546 nm.	Model Rotation 435.8 nm.	Mixture Rotation 546 nm.	Mixture Rotation 435.8 nm.	Deviation 546 nm.	Deviation 435.8 nm.
2.50/0.50	36.53	60.44	35.88	59.24	-0.65	-1.20
2.00/1.00	73.18	121.04	72.22	119.61	-0.96	-1.43
1.50/1.50	109.73	181.39	108.20	178.77	-1.52	-2.62
1.00/2.00	146.77	242.68	145.77	240.95	-1.00	-1.73
0.50/2.50	183.85	303.93	183.22	302.79	-0.63	-1.14

2. Methyl β-D-glucopyranoside (20°C.)

Molarity $ZnCl_2$/Model	Model Rotation 546 nm.	Model Rotation 435.8 nm.	Mixture Rotation 546 nm.	Mixture Rotation 435.8 nm.	Deviation 546 nm.	Deviation 435.8 nm.
2.00/0.50	-7.58	-12.61	-7.83	-12.87	-0.25	-0.26
1.50/1.00	-15.19	-25.18	-15.64	-25.87	-0.45	-0.69
1.25/1.25	-19.02	-31.56	-19.62	-32.42	-0.60	-0.86
1.00/1.50	-22.87	-37.89	-23.45	-38.62	-0.58	-0.75
0.50/2.00	-30.62	-50.78	-31.04	-51.33	-0.42	-0.57

3. Methyl 2,3,4,6-tetra-O-methyl-β-D-glucopyranoside (29°C.)

Molarity $ZnCl_2$/Model	Model Rotation 546 nm.	Model Rotation 435.8 nm.	Mixture Rotation 546.nm.	Mixture Rotation 435.8 nm.	Deviation 546 nm.	Deviation 435.8 nm.
1.00/0.50	-5.17	-8.66	-5.15	-8.75	0.02	-0.09
0.75/0.75	-8.01	-13.58	-7.99	-13.48	0.02	0.10
0.50/1.00	-10.84	-18.32	-10.88	-18.27	-0.04	0.05

4. Methyl 4,6-di-O-methyl-β-D-glucopyranoside (27°C.)

Molarity $ZnCl_2$/Model	Model Rotation 546 nm.	Mixture Rotation 546 nm.	Deviation 546 nm.
1.25/1.25	-13.49	-13.14	0.35

TABLE XIV (Continued)

CONTINUOUS VARIATIONS DATA

Optical Rotation (degrees, two decimeters)

Zinc Chloride-Model Compounds

5. Methyl 3-O-methyl-(α,β)-D-glucopyranoside (27°C.)

Molarity $ZnCl_2$/Model	Model Rotation 546 nm.	Mixture Rotation 546 nm.	Deviation 546 nm.
1.25/1.25	52.14	51.93	-0.21

6. Methyl β-D-xylopyranoside (26°C.)

Molarity $ZnCl_2$/Model	Model Rotation 546 nm.	Mixture Rotation 546 nm.	Deviation 546 nm.
2.00/0.50	-12.46	-12.58	-0.12
1.50/1.00	-24.85	-25.02	-0.17
1.25/1.25	-31.21	-31.45	-0.24
1.00/1.50	-37.40	-37.56	-0.16
0.83/1.67	-41.58	-41.69	-0.11
0.50/2.00	-50.01	-50.08	-0.07

7. Sorbitol (26°C.)

Molarity $ZnCl_2$/Model	Model Rotation 546 nm.	Mixture Rotation 546 nm.	Deviation 546 nm.
1.75/0.25	-0.18	-0.12	0.06
1.50/0.50	-0.39	-0.22	0.17
1.00/1.00	-0.74	-0.50	0.24
0.50/1.50	-1.04	-0.83	0.21
0.25/1.75	-1.19	-1.06	0.13

8. Mannitol (26°C.)

Molarity $ZnCl_2$/Model	Model Rotation 546 nm.	Mixture Rotation 546 nm.	Deviation 546 nm.
0.70/0.20	-0.06	0.00	0.06
0.55/0.35	-0.08	-0.01	0.07
0.45/0.45	-0.11	-0.02	0.09
0.35/0.55	-0.12	-0.06	0.06
0.20/0.70	-0.14	-0.09	0.05

TABLE XV

CONTINUOUS VARIATIONS DATA

Refractive Indices, n_D^{20}

Zinc Chloride-Model Compounds

1. Methyl α-D-glucopyranoside

Molarity $ZnCl_2$/Model	Model	$ZnCl_2$	Refractive Indices Mixture	Deviation
2.50/0.50	1.3458	1.3848	1.3979	0.0003
2.00/1.00	1.3586	1.3762	1.4005	-0.0013
1.50/1.50	1.3715	1.3669	1.4018	-0.0036
1.00/2.00	1.3843	1.3569	1.4069	-0.0013
0.50/2.50	1.3982	1.3455	1.4108	0.0001

Distilled water zero = 1.3330

2. Methyl β-D-glucopyranoside

Molarity $ZnCl_2$/Model	Model	$ZnCl_2$	Refractive Indices Mixture	Deviation
2.00/0.50	1.3450	1.3762	1.3881	-0.0001
1.50/1.00	1.3573	1.3669	1.3908	-0.0004
1.25/1.25	1.3639	1.3623	1.3922	-0.0010
1.00/1.50	1.3700	1.3569	1.3936	-0.0013
0.50/2.00	1.3825	1.3455	1.3952	0.0002

Distilled water zero = 1.3330

3. Methyl 2,3,4,6-tetra-O-methyl-β-D-glucopyranoside

Molarity $ZnCl_2$/Model	Model	$ZnCl_2$	Refractive Indices Mixture	Deviation
1.00/0.50	1.3468	1.3569	1.3701	-0.0012
0.75/0.75	1.3537	1.3520	1.3721	-0.0012
0.50/1.00	1.3610	1.3460	1.3734	-0.0012

Distilled water zero = 1.3324

4. Methanol

Molarity $ZnCl_2$/Model	Model	$ZnCl_2$	Refractive Indices Mixture	Deviation
2.50/0.50	1.3323	1.3848	1.3851	0.0001
2.00/1.00	1.3325	1.3762	1.3764	-0.0002
1.50/1.50	1.3332	1.3669	1.3676	-0.0004
1.00/2.00	1.3355	1.3569	1.3574	-0.0009
0.50/2.00	1.3338	1.3455	1.3472	0.0000

Distilled water zero = 1.3321

TABLE XV (Continued)

CONTINUOUS VARIATIONS DATA

Refractive Indices, n_D^{20}

Zinc Chloride-Model Compounds

5. Ethanol

Molarity $ZnCl_2$/Model	Model	$ZnCl_2$	Refractive Indices Mixture	Deviation
2.50/0.50	1.3337	1.3848	1.3862	-0.0002
2.00/1.00	1.3351	1.3762	1.3787	-0.0005
1.50/1.50	1.3367	1.3669	1.3704	-0.0011
1.00/2.00	1/3382	1.3569	1.3619	-0.0011
0.50/2.00	1.3401	1.3455	1.3513	-0.0004

Distilled water zero = 1.3321

6. n-Propanol

Molarity $ZnCl_2$/Model	Model	$ZnCl_2$	Refractive Indices Mixture	Deviation
2.50/0.50	1.3348	1.3848	1.3872	-0.0003
2.00/1.00	1.3378	1.3762	1.3807	-0.0010
1.50/1.50	1.3407	1.3669	1.3738	-0.0017
1.00/2.00	1.3431	1.3569	1.3667	-0.0012
0.50/2.50	1.3466	1.3455	1.3592	-0.0008

Distilled water zero = 1.3321

7. Ethylene Glycol

Molarity $ZnCl_2$/Model	Model	$ZnCl_2$	Refractive Indices Mixture	Deviation
2.50/0.50	1.3350	1.3848	1.3873	-0.0004
2.00/1.00	1.3381	1.3762	1.3813	-0.0009
1.50/1.50	1.3409	1.3669	1.3747	-0.0010
1.00/2.00	1.3439	1.3569	1.3678	-0.0009
0.50/2.50	1.3469	1.3455	1.3598	-0.0005

Distilled water zero = 1.3321

8. Glycerol

Molarity $ZnCl_2$/Model	Model	$ZnCl_2$	Refractive Indices Mixture	Deviation
2.50/0.50	1.3377	1.3848	1.3900	-0.0004
2.00/1.00	1.3430	1.3762	1.3860	-0.0011
1.50/1.50	1.3484	1.3669	1.3819	-0.0013
1.00/2.00	1.3538	1.3569	1.3775	-0.0011
0.50/2.50	1.3591	1.3455	1.3720	-0.0005

Distilled water zero = 1.3321

TABLE XVI

NMR CHEMICAL SHIFT ASSIGNMENTS

(At standard operating temperature, ~40°C.)

1. Methyl α-D-glucopyranoside

Proton Peaks	Chemical Shift Assignments, c.p.s. 1.0M Model	1.0M Model +1.0M $ZnCl_2$
H_1 (anomeric proton)	286.30	287.60
$H_{2,3,4,5}$ (ring protons)	213.85	215.25
H_{OCH_3} (methoxy protons)	202.75	202.95

2. Methyl β-D-glucopyranoside

Proton Peaks	0.5M Model	Chemical Shift Assignments, c.p.s. 0.5M Model +0.5M $ZnCl_2$	1.0M Model +1.0M $ZnCl_2$	1.5M Model +1.5M $ZnCl_2$
H_1	260.15	262.20	262.20	262.15
H_{OCH_3}	211.55	212.75	212.35	212.10
$H_{2,3,4,5}$	203.35	205.05	205.10	205.05

3. Methyl 2,3,4,6-tetra-O-methyl-β-D-glucopyranoside

Proton Peaks	Chemical Shift Assignments, c.p.s. 1.0M Model	1.0M Model +1.0M $ZnCl_2$
H_1	257.30	257.40
H_{OCH_3} protons		
A	213.85	213.90
B	210.10	210.00
C	208.50	208.45
D	201.25	201.05
$H_{2,3,4,5}$ protons		
E	193.80	193.80
F	186.95	186.75
G	179.40	179.35

TABLE XVI (Continued)

NMR CHEMICAL SHIFT ASSIGNMENTS

(At standard operating temperature ~40°C.)

4. Methyl 4,6-di-O-methyl-β-D-glucopyranoside

Proton Peaks	Chemical Shift Assignments, c.p.s. 0.5M Model	0.5M Model +0.5M $ZnCl_2$
H_1	257.70	259.50
H_{OCH_3} protons		
A	210.50	210.90
B	202.70	203.30
$H_{2,3,4,5}$	204.90	206.55

5. Methyl 3-O-methyl-(α,β)-D-glucopyranoside

Proton Peaks	Chemical Shift Assignments, c.p.s. 0.5M Model	0.5M Model +0.5M $ZnCl_2$
$H_1(\alpha)$	285.55	285.65
$H_1(\beta)$	260.80	261.40
H_{OCH_3} (3-O-methoxy)	213.90	213.90
H_{OCH_3} (β-glycosidic)	212.05	212.15
H_{OCH_3} (α-glycosidic)	203.55	203.30
$H_{2,3,4,5}$ protons		
A	208.65	208.85
B	206.80	206.95

TABLE XVI (Continued)

NMR CHEMICAL SHIFT ASSIGNMENTS

(At standard operating temperature ~40°C.)

6. Ethyl 3,4,6-tri-O-methyl-β-D-glucopyranoside

Proton Peaks	Chemical Shift Assignments, c.p.s. 0.5M Model	0.5M Model +0.5M $ZnCl_2$
H_1	263.00	263.20
H_{OCH_3} protons		
A	214.90	214.65
B	209.90	209.75
C	201.95	201.90
$H_{2,3,4,5}$ protons		
D	197.90	197.95
E	194.70	194.60

7. Methyl 6-deoxy-β-D-glucopyranoside

Proton Peaks	Chemical Shift Assignments, c.p.s. 1.0M Model	1.0M Model +1.0M $ZnCl_2$
H_1	258.05	260.35
H_{OCH_3}	209.75	210.20
$H_{2,3,4,5}$ protons		
A	206.05	208.00
B	198.80	199.75
C	192.90	194.55
D	184.05	185.20

TABLE XVI (Continued)

NMR CHEMICAL SHIFT ASSIGNMENTS

(At standard operating temperature ~40°C.)

8. Methyl β-D-xylopyranoside

Proton Peaks	Chemical Shift Assignments, c.p.s. 0.5M Model	0.5M Model +0.5M $ZnCl_2$	1.5M Model +1.5M $ZnCl_2$
H_1	256.60	258.25	258.60
H_{OCH_3}	209.55	210.15	210.15
$H_{2,3,4,5}$ protons			
A	240.10	241.00	240.75
B	231.45	232.75	232.30
C	227.40	228.35	228.35
D	220.25	221.50	221.50
E	203.45	205.35	205.60
F	194.50	195.90	195.80
G	192.50	193.90	193.80

9. Hexa-O-methyl-myo-inositol

Proton Peaks	Chemical Shift Assignments, c.p.s. 1.0M Model	1.0M Model +1.0M $ZnCl_2$
Ring protons		
A	247.50	247.75
B	196.95	196.65
Methoxy protons		
C	212.95	212.50
D	210.35	210.00
E	206.50	206.55

TABLE XVI (Continued)

NMR CHEMICAL SHIFT ASSIGNMENTS

(At standard operating temperature, ~40°C.)

10. myo-Inositol

Proton Peaks	Chemical Shift Assignments, c.p.s. 1.0M Model	0.5M Model +0.5M $ZnCl_2$	1.5M Model +1.5M $ZnCl_2$
Ring protons			
A	242.00	243.00	242.95
B	218.80	219.55	219.65
C	215.80	216.75	216.70
D	211.35	212.50	212.60
E	202.10	203.65	203.95
F	192.70	194.05	194.15

11. Sorbitol

Proton Peaks	Chemical Shift Assignments, c.p.s. 1.0M Model	0.5M Model +0.5M $ZnCl_2$	1.5M Model +1.5M $ZnCl_2$
Chain protons			
A	228.20	230.25	229.95
B	225.65	227.80	227.85
C	221.25	222.90	223.00

12. Glycerol

Proton Peaks	Chemical Shift Assignments, c.p.s. 1.0M Model	0.5M Model +0.5M $ZnCl_2$	1.5M Model +1.5M $ZnCl_2$
Main peak of spectrum	214.95	216.85	216.85

13. Ethylene Glycol

Proton Peaks	Chemical Shift Assignments, c.p.s. 1.0M Model	0.5M Model +0.5M $ZnCl_2$	1.5M Model 1.5M $ZnCl_2$
H_{CH_2OD}	217.05	217.75	218.35

TABLE XVI (Continued)

NMR CHEMICAL SHIFT ASSIGNMENTS

(At standard operating temperature, ~40°C.)

14. Methyl Cellosolve

Proton Peaks	Chemical Shift Assignments, c.p.s.		
	1.0M Model	0.5M Model +0.5M $ZnCl_2$	1.5M Model +1.5M $ZnCl_2$
H_{CH_2OD}	217.45	218.15	218.45
H_{CH_2}	214.95	215.70	216.00
H_{CH_3}	200.20	201.05	201.50

15. Ethanol

Proton Peaks	Chemical Shift Assignments, c.p.s.		
	1.0M Model	0.5M Model +0.5M $ZnCl_2$	1.5M Model +1.5M $ZnCl_2$
H_{CH_2OD}	216.35	217.30	217.55
H_{CH_3}	68.65	68.95	69.40

16. n-Propanol

Proton Peaks	Chemical Shift Assignments, c.p.s.		
	1.0M Model	0.5M Model +0.5M $ZnCl_2$	1.5M Model +1.5M $ZnCl_2$
H_{CH_2OD}	212.05	211.65	212.05
H_{CH_2}	88.25	88.00	88.10
H_{CH_3}	52.00	52.15	52.05

TABLE XVII

TEMPERATURE DEPENDENCY OF THE NMR CHEMICAL SHIFT OF METHYL β-D-GLUCOPYRANOSIDE AS A FUNCTION OF THE ZINC CHLORIDE CONCENTRATION

Zinc Chloride Molarity	Chemical Shift Assignments, c.p.s. Anomeric Proton (H_1)			Ring Protons ($H_{2,3,4,5}$)		
	42°C.	47°C.	68°C.	42°C.	47°C.	68°C.
0.0	260.69	260.06	259.00	203.75	203.25	202.92
7.0	267.73	267.31	265.94	211.75	211.31	210.44
	43°C.	60°C.	77°C.	43°C.	60°C.	77°C.
0.0	260.44	259.91	258.56	203.75	203.56	202.94
8.0	268.75	267.25	265.56	212.66	211.75	210.81
8.5	269.31	267.97	266.62	--	--	--
9.0	269.94	268.25	266.94	--	--	--

TABLE XVIII

ULTRAVIOLET ABSORBANCES

1. Methyl β-D-glucopyranoside (ten centimeter cell)

Wavelength, nm.	1.0M Model	1.0M $ZnCl_2$	1.0M Model +1.0M $ZnCl_2$
220	0.650	1.392	1.957
225	0.579	1.010	1.495
230	0.513	0.871	1.286
235	0.450	0.870	1.228
240	0.405	0.964	1.289
245	0.372	1.085	1.400
250	0.342	1.197	1.485
255	0.322	1.243	1.510
260	0.305	1.195	1.436
265	0.292	1.037	1.246
270	0.280	0.801	0.994
275	0.270	0.567	0.745
280	0.259	0.375	0.560
290	0.237	0.185	0.336
300	0.220	0.110	0.238
310	0.200	0.078	0.189
320	0.182	0.062	0.152
330	0.159	0.049	0.124
340	0.139	0.035	0.104

2. Methyl β-D-glucopyranoside (one centimeter cell)

Molarities Model/$ZnCl_2$	Absorbances at 255 nm.		
	Model	$ZnCl_2$	Mixture
0.5/3.0	0.030	0.167	0.197
0.5/5.0	0.030	0.285	0.315
0.5/6.0	0.030	0.360	0.400
0.5/7.0	0.030	0.582	0.588
0.5/9.0	0.030	0.860	1.010
0.5/10.0	0.030	0.970	1.210

APPENDIX II

PREPARATION OF MODEL COMPOUNDS

This section describes the synthesis and/or purification of the various model compounds which were used in the experimental procedures with zinc chloride. It should be noted that none of the experimental procedures required very high purity; therefore, extensive purifications and characterizations were not attempted.

METHYL α-D-GLUCOPYRANOSIDE

Methyl α-D-glucopyranoside from the Pfanstiehl Chemical Company was purified by three successive crystallizations from absolute ethanol. The melting point and specific optical rotation ($[\alpha]_D^{20}$) were 167-168°C. and 159.13 degrees, respectively; literature values (50) were 167°C. and 158-159 degrees, respectively.

METHYL β-D-GLUCOPYRANOSIDE

Methyl β-D-glucopyranoside from the Pfanstiehl Chemical Company was purified by two successive crystallizations from absolute ethanol. The melting point and specific optical rotation ($[\alpha]_D^{20}$) were 108-109°C. and -32.64 degrees, respectively; literature values (50) were from 104 to 109-111°C. and -32.5 degrees, respectively.

METHYL 2,3,4,6-TETRA-O-METHYL-β-D-GLUCOPYRANOSIDE

Methyl 2,3,4,6-tetra-O-methyl-β-D-glucopyranoside was prepared by methylating methyl β-D-glucopyranoside with dimethyl sulfate following the method of West and Holden (51). Purification was accomplished by a fractional distillation in a spinning band column at reduced pressure (0.3 mm.). Purified yield was 53%. The melting point and specific optical rotation ($[\alpha]_D^{20}$) were 37-38°C. and -17.3 degrees, respectively; literature values (50) were 40-41°C. and -17.3 degrees, respectively.

METHYL 4,6-di-O-METHYL-β-D-GLUCOPYRANOSIDE

Several grams of methyl 4,6-di-O-methyl-β-D-glucopyranoside prepared by G. Fredrick Bayer (19) (crop number one) were used. The material had a melting point of 77-78°C. compared to a literature value of 77-79°C. (50).

METHYL 3-O-METHYL-(α,β)-D-GLUCOPYRANOSIDE

Methyl 3-O-methyl-(α,β)-D-glucopyranoside was synthesized from 3-O-methyl glucopyranose by reaction with methanol in the presence of IR-120 resin following the method of Bayer (19). The reducing sugars were removed from the product by treatment with hot alkali. The sirup which resulted after removal of ions with a mixed bed resin (MB-3) was used without further purification. NMR spectra indicated that the compound was about 90% alpha anomer.

myo-INOSITOL

Pharmaceutical grade (No. 4071) myo-inositol produced by Calbiochem Company was used without further purification.

HEXA-O-METHYL-myo-INOSITOL

Hexa-O-methyl-myo-inositol was prepared by two successive methylations of myo-inositol with dimethyl sulfate following the method of West and Holden (51). A comparison of the NMR spectra of the product in chloroform and in deuterium oxide indicated no exchangeable protons; i.e., an absence of hydroxyl peaks. This product was used without further purification.

ETHYL 3,4,6-TRI-O-METHYL-β-D-GLUCOPYRANOSIDE

A sample of ethyl 3,4,6-tri-O-methyl-β-D-glucopyranoside prepared by D. Hultman (53) was used. The melting point and specific optical rotation in chloroform were 52-53.5°C. and -23.8 degrees, respectively.

METHYL β-D-XYLOPYRANOSIDE

Methyl β-D-xylopyranoside produced by Pfanstiehl Chemical Company was used without further purification. The melting point and specific optical rotation ($[\alpha]_D^{20}$) were 156-158°C. and -65.5 degrees, respectively.

METHYL 6-DEOXY-β-D-GLUCOPYRANOSIDE

Methyl 6-deoxy-β-D-glucopyranoside produced by Pierce Chemical Company was used without further purification.

A number of model compounds were purchased and used without further purification. These compounds are listed in Table XIX.

TABLE XIX

COMPOUNDS USED WITHOUT PURIFICATION

Model Compound	Chemical Company	Grade
Mannitol	Pfanstiehl	c.p.
Sorbitol	Pfanstiehl	c.p.
Glycerol	Matheson, Coleman, and Bell	Reagent
Ethylene Glycol	Mallinckrodt	Reagent
Methyl Cellosolve	Eastman	Unknown
Methanol	Commercial Solvents	Reagent
Ethanol	Commercial Solvents	Reagent
n-Propanol	Fisher	Reagent

APPENDIX III

ANALYSIS OF EXPERIMENTAL ERROR

OPTICAL ROTATION DATA

The error due to the variation of optical rotation measurements on the same sample was negligible compared to that between duplicate solutions due to errors in preparing the solutions. Table XX presents a typical case; that of the optical rotation data (546 nm.) for the continuous variations experiment with methyl β-D-glucopyranoside and zinc chloride.

TABLE XX

VARIANCE OF OPTICAL ROTATION MEASUREMENTS
(AT 546 nm.)

Molarities		Optical	Mean Value	Variance,	
Model	$ZnCl_2$	Rotation	Between Pairs	$\underline{V}$	$\underline{V}^2$
0.50	--	-7.61	-7.575	0.035	0.00123
0.50	--	-7.54		0.035	0.00123
1.00	--	-15.19	-15.185	0.005	0.00003
1.00	--	-15.18		0.005	0.00003
1.25	--	-19.01	-19.020	0.010	0.00010
1.25	--	-19.03		0.010	0.00010
1.50	--	-22.87	-22.865	0.005	0.00003
1.50	--	-22.86		0.005	0.00003
2.00	--	-30.54	-30.615	0.075	0.00563
2.00	--	-30.69		0.075	0.00563
0.50	2.00	-7.83	-7.825	0.005	0.00003
0.50	2.00	-7.82		0.005	0.00003
1.00	1.50	-15.65	-15.640	0.010	0.00010
1.00	1.50	-15.63		0.010	0.00010
1.25	1.25	-19.67	-19.615	0.055	0.00250
1.25	1.25	-19.56		0.055	0.00250
1.50	1.00	-23.49	-23.450	0.040	0.00160
1.50	1.00	-23.41		0.040	0.00160
2.00	0.50	-31.04	-31.040	0.000	0.00000
2.00	0.50	-31.04		0.000	0.00000

The standard deviation may be calculated from the variance.

$$\sigma = \sqrt{\sum v^2/(n-1)} = \sqrt{0.01512/19} = 0.03 \text{ degree}$$

Any deviation in optical rotation between two values greater than $(2)(1.96)(\sigma)/\sqrt{N}$ is significant at the 95% confidence level. Since all values of the optical rotations data are for two or more identical solutions, any deviation greater than $(2)(1.96)(0.03)/\sqrt{2} = 0.08$ degree is significant at the 95% level. On this basis, essentially all the optical rotations deviations observed in this thesis qualify as significant to the 95% confidence level or greater.

NMR CHEMICAL SHIFT MEASUREMENTS

Table XXI contains the results of eleven NMR spectra for the same 1.0M methyl β-D-glucopyranoside solution in deuterium oxide with DSS as an internal reference. These spectra were obtained during a time interval of three hours. Amplitude was varied from 4.0-16.0 and the spinning rate as well as the detector phase setting was changed slightly for each spectrum.

TABLE XXI

DUPLICATE CHEMICAL SHIFT MEASUREMENTS

Chemical Shift Assignments, c.p.s.

Anomeric Proton (H_1)	Methoxy Proton (H_{OCH_3})	Ring Protons ($H_{2,3,4,5}$)
260.75	212.00	203.75
261.00	212.25	204.00
260.75	211.75	203.75
261.00	212.25	204.00
261.00	212.25	204.00
261.25	212.00	204.00
261.25	212.00	204.00
261.00	212.00	204.00
261.25	212.00	203.75
260.75	211.75	203.75
261.00	211.75	204.00

The standard deviations of the chemical shift assignments for H_1, H_{OCH_3}, and $H_{2,3,4,5}$ are 0.19, 0.19, and 0.16 c.p.s., respectively, with an average of 0.18 c.p.s.

Since all values of the chemical shift assignments are for five or more identical spectra, any deviation greater than $(2)(1.96)(0.18)/\sqrt{5} = 0.32$ c.p.s. is significant at the 95% confidence level.

APPENDIX IV

SAMPLE CALCULATIONS

CONTINUOUS VARIATIONS DATA

OPTICAL ROTATION DEVIATION

The following data are from Table XIV for methyl β-D-glucopyranoside.

Molarity $ZnCl_2$/Model	Model Rotation 546 nm.	Mixture Rotation 546 nm.
1.25/1.25	-19.02	-19.62

Deviation = (Mixture Rotation) - (Model Rotation)

= -19.62 - (-19.02) = -0.62 degree

REFRACTIVE INDEX DEVIATION

The following data are from Table XV for methyl β-D-glucopyranoside.

Molarity $ZnCl_2$/Model	Refractive Indices, n_D^{20} Model	$ZnCl_2$	Mixture
1.25/1.25	1.3639	1.3623	1.3922

Distilled water zero = 1.3330

$$\text{Deviation} = (n_{mixture}) - (n_{ZnCl_2}) - (n_{model}) + (n_{H_2O})$$

$$= 1.3922 - 1.3623 - 1.3639 + 1.3330 = -0.0010$$

NMR CHEMICAL SHIFT CHANGE

The following data for methyl β-D-glucopyranoside are from Table XVI.

Proton Peaks	Chemical Shift Assignments, c.p.s. 1.0M Model	0.5M Model +0.5M $ZnCl_2$
H_1	260.15	262.20

$$\Delta\nu = (\nu_{model+ZnCl_2}) = (\nu_{model}) - 262.20 - 260.15 = 2.05 \text{ c.p.s.}$$

ULTRAVIOLET ABSORBANCE DEVIATION

The following data are for methyl β-D-glucopyranoside from Table XVIII.

Wavelength, nm.	1.0M Model	1.0M $ZnCl_2$	1.0M Model +1.0M $ZnCl_2$
255	0.322	1.243	1.510

$$\text{Deviation} = (A_{\text{model}+ZnCl_2}) - (A_{\text{model}}) - (A_{ZnCl_2})$$
$$= 1.510 - 0.322 - 1.243 = -0.055$$

CALCULATED REQUIRED RATIO OF WATER TO ZINC

The following data are taken from Table X.

Stoichiometric Zinc Chloride Concentration		$ZnCl_4(H_2O)_2^{--}$	$Zn(H_2O)_6^{++}$
wt. %	Molarity	Molarity	Molarity
60	7.70	2.70	5.00

Required molar ratio of water to zinc is:

$$[(H_2O)/Zn]_{req.} = [(2.70)(2) + (5.00)(6)]/7.70 = 4.60$$

EFFECT OF TEMPERATURE ON THE NMR CHEMICAL SHIFT CHANGE ($\Delta\nu$)

The following table of data for deuterium oxide was obtained from the Handbook of Chemistry and Physics (52). All the calculations are based on Equation (7) (page 13.).

TABLE XXII

EFFECT OF TEMPERATURE ON THE DIELECTRIC CONSTANT OF D_2O

t, °C.	ε	$-d\varepsilon/dt$	$\left(\frac{1}{\varepsilon}\right)\left(\frac{d\varepsilon}{dt}\right) \times 10^3$
40	72.735	0.3344	4.597
45	71.083	0.3265	4.593
50	69.470	0.3187	4.587
55	67.896	0.3112	4.583
60	66.358	0.3038	4.578

Since methyl β-D-glucopyranoside is a solid in the temperature range (43-77°C.), then n is essentially a constant. Also μ and cos φ are constants. Therefore $d(\Delta\nu)/dt$ is a function of the ratio of $(\varepsilon-1)/(2\varepsilon+n^2)$. The calculations presented in Table XXIII illustrate that $d(\Delta\nu)/dt$ is essentially independent of temperature.

TABLE XXIII

EFFECT OF TEMPERATURE ON $(\varepsilon-1)/(2\varepsilon+n^2)$

Assumed Initial Dielectric Constant (ε_t = 43°C.)	(ε_t = 60°C.)	$\frac{(\varepsilon_{43}-1)}{(2\varepsilon_{43}+n^2)}$ (Q_1)	$\frac{(\varepsilon_{60}-1)}{(2\varepsilon_{60}+n^2)}$ (Q_2)	Q_2/Q_1
71.744[a]	66.358[a]	0.485	0.484	0.998
50	46.12	0.478	0.477	0.997
20	18.45	0.448	0.444	0.991
10	9.22	0.401	0.394	0.982

[a]Values from Table XXII.

$n^2 \cong 2.5$

APPENDIX V

SAMPLE SPECTRA

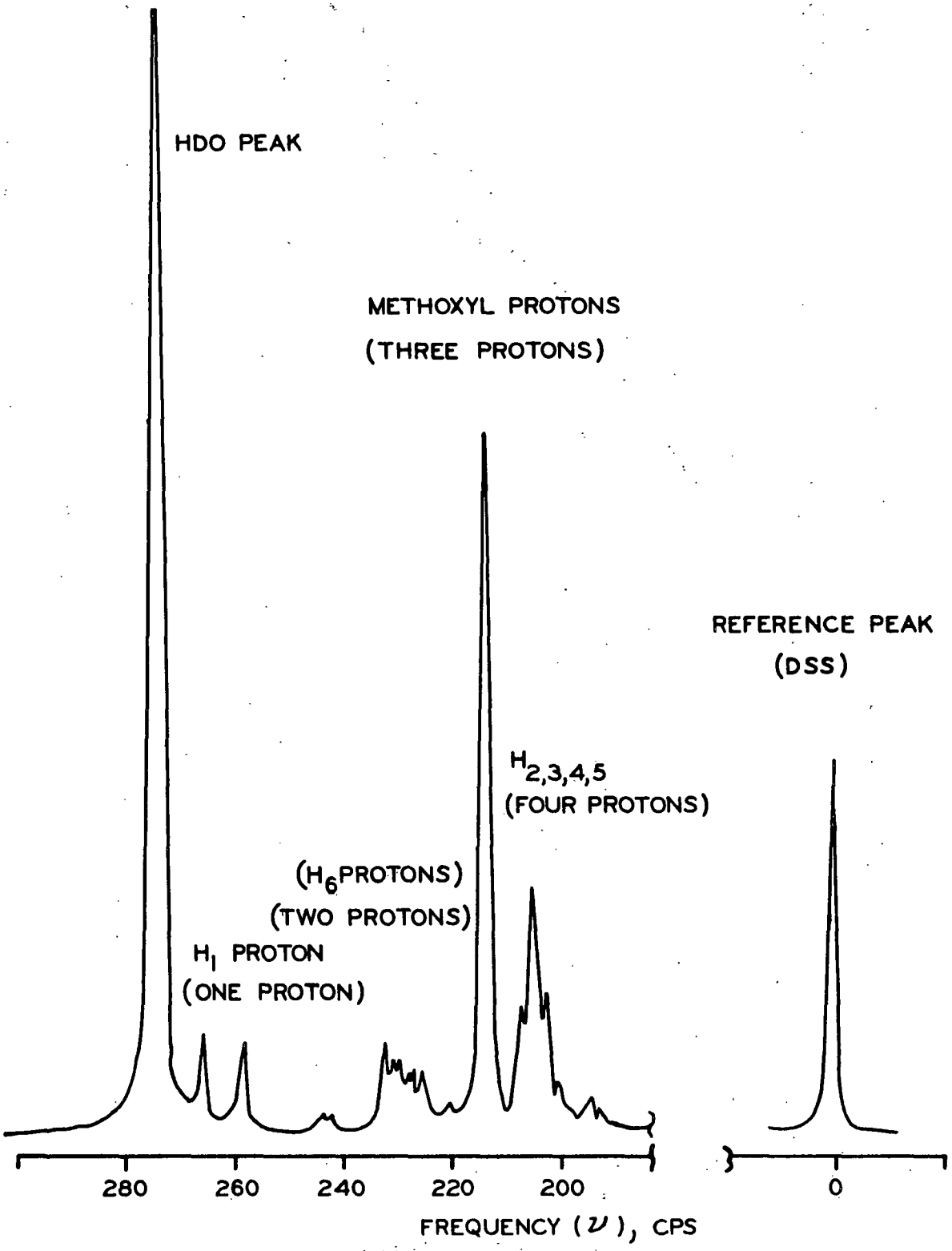

Figure 10. NMR Spectrum of Methyl β-D-glucopyranoside

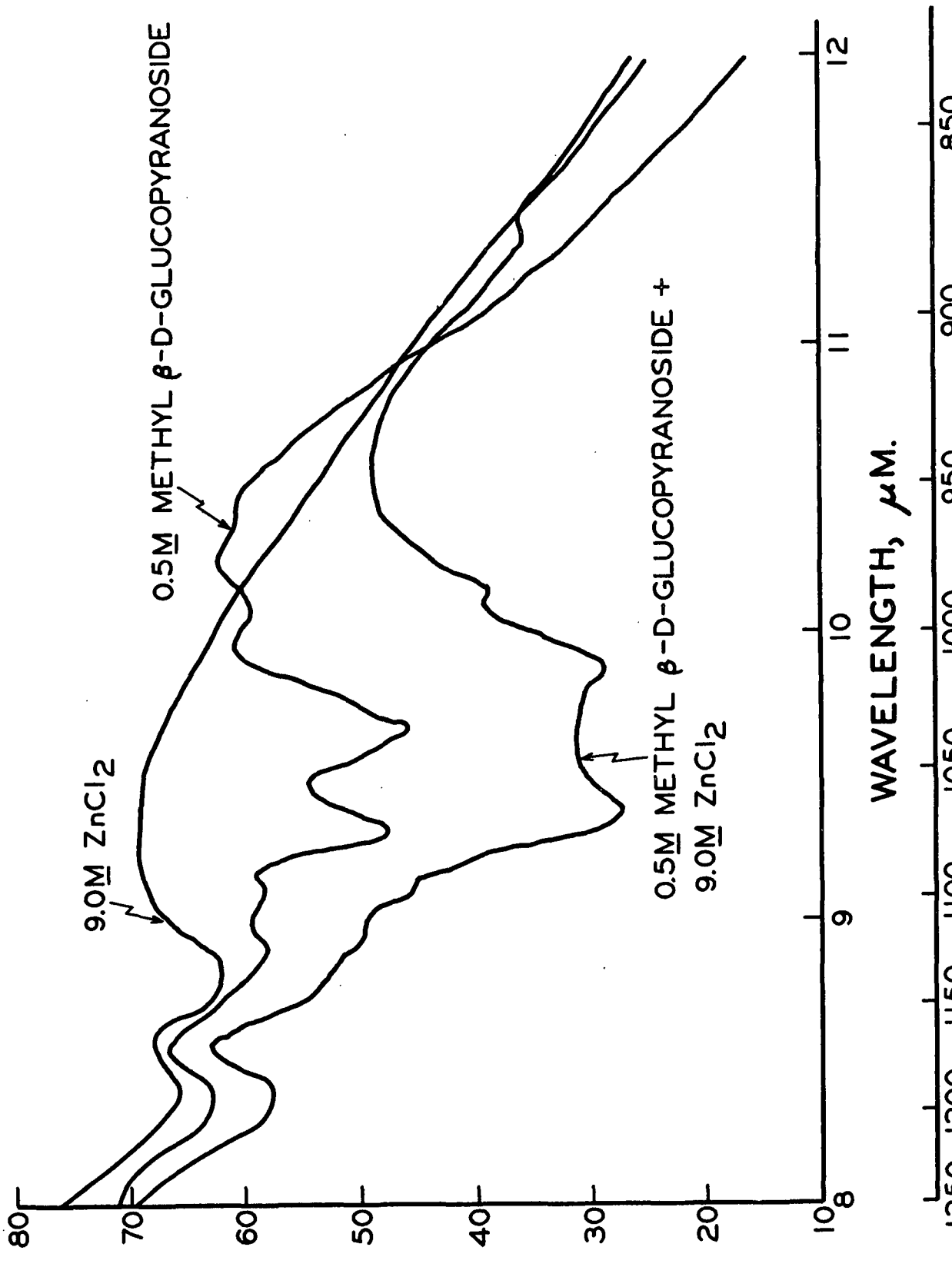

Figure 1. Infrared Spectra of Methyl β-D-Glucopyranoside and Zinc Chloride

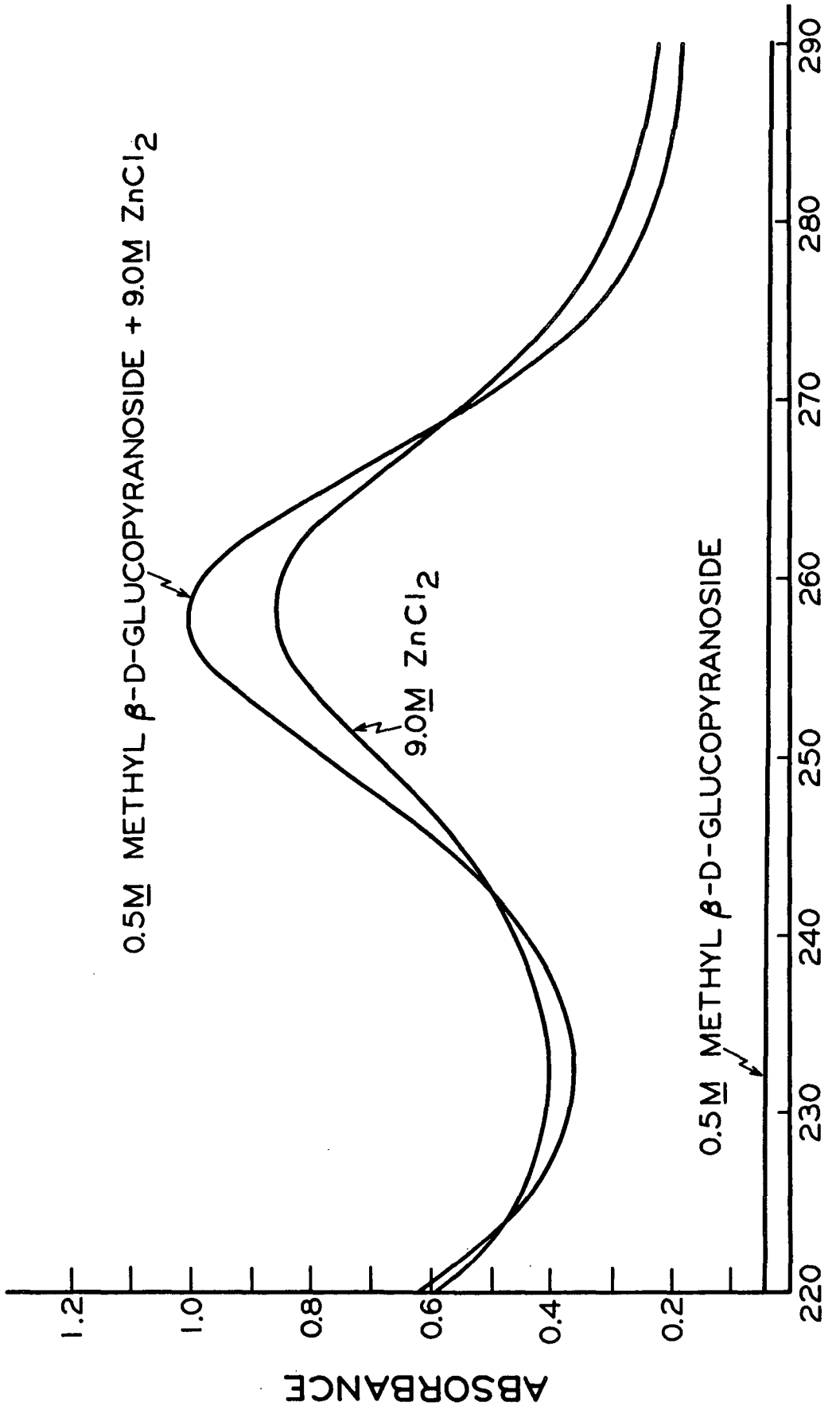

Figure 12. Ultraviolet Spectra of Methyl β-D-glucopyranoside and Zinc Chloride